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# The Journal *of the* Society of Dyers and Colourists

Volume 76



Number 5

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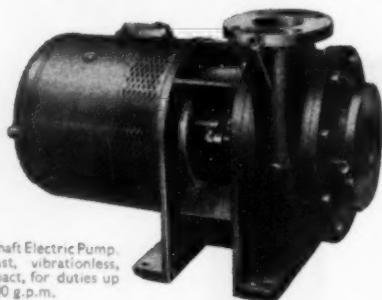
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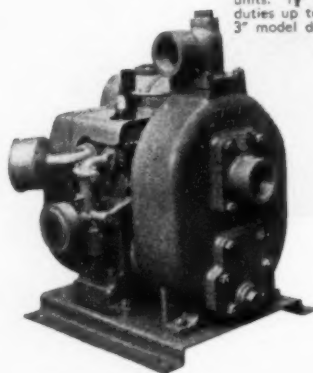


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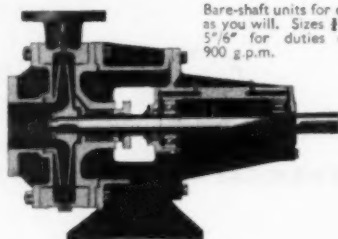
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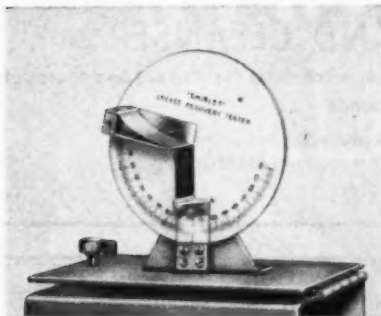
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Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1-10 of the January 1960 and pages 341-348 of the July 1959 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (Telephone Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

### Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

#### LECTURES

The Dyeing of Wool by Solvent-assisted Processes *W. Beal, K. Dickinson, and E. Bellhouse*

#### COMMUNICATIONS

Quinonoid Dyes. XIV—Relation between Coplanarity and Substantivity of Quinonoid Dyes to Secondary Cellulose Acetate Rayon and Cellulosic Fibres

*E. H. Daruwalla, S. S. Rao, and B. D. Tilak*

The English Contribution to the Early History of Indigo Printing

*P. C. Floud*

The English Contribution to the Development of Copper-plate Printing

*P. C. Floud*

The Chemistry of Esters of Leuco Vat Dyes

IV—Oxidation with Solutions of Nitrous Acid

*A. Johnson and A. P. Lockett*

Relation of Apparent Diffusion Coefficient to the Time of Half-dyeing

*W. F. Kilby*

The Radiation-induced Graft Copolymerisation of Methacrylic Acid to Nylon

*R. Roberts and J. K. Thomas*

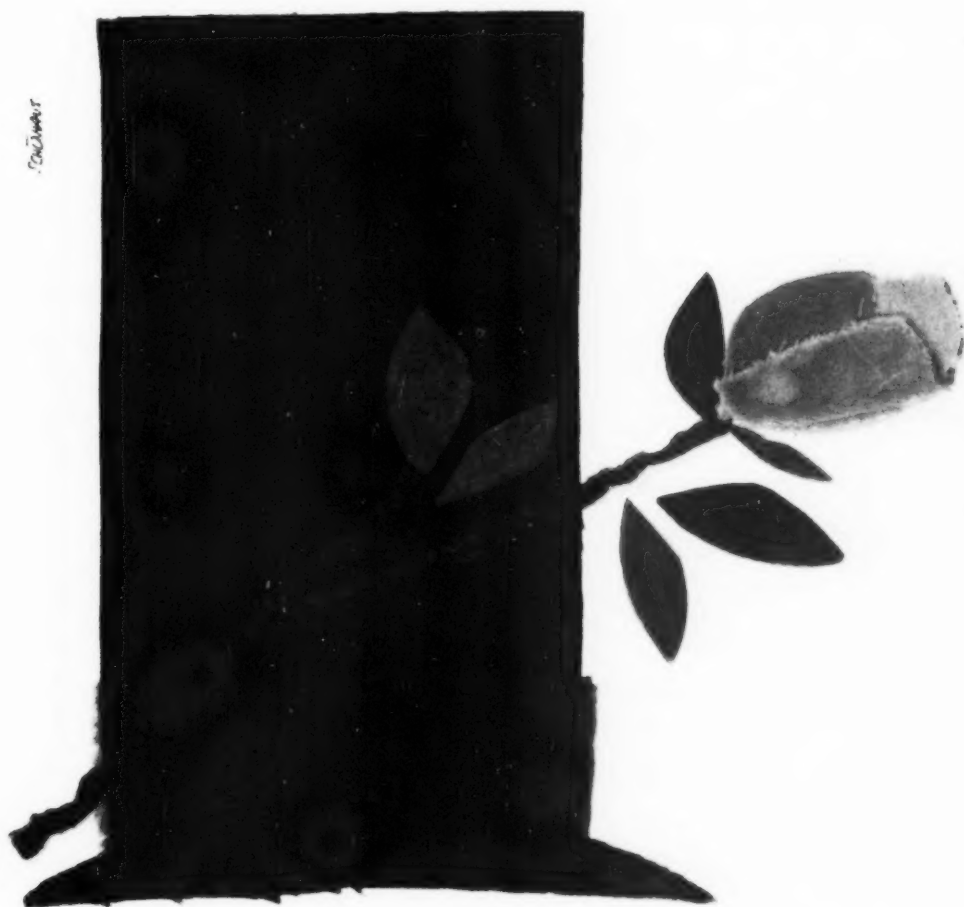
#### I.F.A.T.C.C. 1959 CONGRESS PAPER

A New One-bath Method for Continuous or Pad-Roll Vat Dyeing

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# THE JOURNAL

OF THE

## Society of Dyers and Colourists

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Volume 76 Number 5

MAY 1960

Issued Monthly

### Proceedings of the Society

#### The Alkaline Degradation of Chemically Modified Cellulose

W. M. CORBETT

*Meeting of the Manchester Section held at the Textile Institute on 29th May 1959,  
Mr. H. A. Turner in the chair*

A review is presented of recent work on the alkaline degradation of mono- and poly-saccharide derivatives which are structurally similar to oxidised celluloses. The importance of a  $\beta$ -alkoxy-carbonyl elimination reaction is emphasised, and it is shown how such a reaction explains the occurrence of a chain-scission reaction in alkali-treated oxidised celluloses, as well as the formation of several of the acidic products.

#### INTRODUCTION

The alkaline degradation of cellulose and of oxidised cellulose is of considerable importance to the many industries using cellulose or its derivatives, especially to the textile industry. The degradation of cellulose by alkali at normal temperatures causes very little weight-loss and has little effect on the degree of polymerisation (D.P.), and can usually be disregarded. However, if the cellulose is oxidised prior to or during alkaline treatment, a very different state of affairs exists. Oxidised celluloses (oxycelluloses) are extremely sensitive to alkali and undergo a chain-scission which results in a rapid fall of D.P. and considerable weight-loss. Thus, Davidson<sup>1</sup> has shown that, although little chain-scission occurs during mild oxidation under acidic conditions (the D.P. of the nitrates of oxycelluloses are similar to those of the original cellulose), the D.P. of an oxycellulose in cuprammonium hydroxide falls rapidly. Use is made of this chain-scission in order to modify cellulose, as in the alkali-ageing of alkali cellulose, a process to reduce the D.P. before forming derivatives. In some instances chain-scission of the cellulose molecules may be an undesired reaction and efforts are made to eliminate it. Examples of this are the alkaline breakdown or "tendering" of photo-oxidised or of excessively bleached fabrics.

Since the end of the last century, workers throughout the world have been engaged on the elucidation of the mechanism of the alkaline degradation of oxycelluloses. It was observed<sup>2</sup> that the group responsible for degradation was a carbonyl group, either in the form of an aldehyde (produced by oxidation of the primary alcohol group at C<sub>(6)</sub> or by a carbon-carbon scission at

C<sub>(2)</sub>-C<sub>(3)</sub> of a glucose repeating unit) or as a ketone (produced by oxidation of a secondary alcohol group at C<sub>(2)</sub> or C<sub>(3)</sub>). If this carbonyl group is removed, either by reduction to an alcohol by a reagent such as sodium borohydride<sup>3</sup>, or, in the case of an aldehyde, by oxidation to an acid by a reagent such as chlorous acid<sup>4</sup>, the oxycellulose becomes relatively stable towards alkali. Modification of cellulose, and indeed any polysaccharide, so as to increase the number of carbonyl or potential carbonyl groups, causes the polysaccharide to become more sensitive towards alkali. An increase in the number of carbonyl groups may be achieved by oxidation, hydrolysis by acid or by alkali at high temperatures, or by denitration under non-reducing conditions. It is the alkaline degradation of such modified celluloses that is discussed in this paper, but it must be remembered that other types of modified celluloses, e.g. the partial ethers and esters, in which some of the unreacted hydroxyl groups have undergone oxidation, will also undergo alkaline degradation in a somewhat similar manner.

Oxidation of a glucose repeating unit of cellulose without chain-scission of the molecule may occur at the hydroxyl groups at C<sub>(2)</sub>, C<sub>(3)</sub> or C<sub>(6)</sub>. Wherever oxidation occurs, the main features of any alkali-sensitive glucose repeating unit are a carbonyl group and a glucosidic link. The simplest compounds containing both features are the disaccharides, and consequently the action of alkali upon these compounds has been studied. The work was extended to cover the monomethyl ethers of glucose having the ether group in various positions; these derivatives have the necessary requirements and, in some cases, are more readily obtainable than the corresponding disaccharides.

In the following review, only the more important reactions are discussed, and side reactions are ignored unless they are of importance when considering the alkaline degradation of cellulose and chemically modified cellulose<sup>5</sup>.

#### MONOSACCHARIDE DERIVATIVES

The simplest type of model compound is a 3-*O*-substituted aldose such as laminaribiose (3-*O*-β-D-glucosyl-D-glucose (I) and 3-*O*-methyl-D-glucose (II). It was observed that laminaribiose in lime-water readily degraded to one mole of glucose and one equivalent of acid per mole of disaccharide decomposed<sup>6</sup> (Fig. 1). In the later stages of the reaction the glucose decomposed to further acids. Isolation of the acid product produced in the early stages of the reaction showed that it was essentially metasaccharinic acid (III). The 3-methyl ether of D-glucose behaved in an

analogous manner, except that methanol was produced instead of glucose<sup>7</sup>. The series of reactions leading to the elimination of the substituent group and the ultimate formation of metasaccharinic acid can be readily explained by application of the mechanisms proposed by Isbell<sup>8</sup> to explain the formation of saccharinic acids in alkaline solutions of unsubstituted monosaccharides. Thus, according to Isbell's theory (Fig. 2), a 3-*O*-substituted glucose in alkaline solution first ionises to give the ion (IV), which then undergoes an electron transference resulting in the elimination of the substituent group at C<sub>3</sub> and the formation of the enol (V). The latter is the enol of the dicarbonyl compound (VI) with which it is in equilibrium. Finally, the dicarbonyl compound is postulated to undergo the well known "benzile acid" rearrangement, the nature of which is still uncertain, to give metasaccharinic acid. At present none of the intermediates of the reaction has been isolated, so there is no conclusive proof that the postulated series of reactions is correct.

In the 3-*O*-substituted ketoses such as turanose<sup>6</sup> (3-*O*-α-D-glucosyl-D-fructose, VII) and 3-*O*-methyl-D-fructose<sup>7</sup> (VIII), the substituent is in an α-position to the carbonyl group, so elimination of the hydroxyl group on C<sub>4</sub> would be expected giving rise to a new acid. Elimination of the hydroxyl group may occur, but it has not been detected. This is not surprising: it would be relatively slow since it requires the elimination of a hydroxyl ion in an environment already containing hydroxyl ions. Instead, the ketose derivatives isomerise by a Lobry de Bruyn-Alberda van Ekenstein transformation<sup>9</sup> to the corresponding aldose derivatives which then degrade as described above (Fig. 1). The acid yield is somewhat higher in this case owing to the formation of lactic acid.

Isbell's mechanism also explains the degradation products produced when 4-*O*-substituted derivatives of aldoses and ketoses are treated with alkali (Fig. 3). 4-*O*-Derivatives of fructose such as maltulose<sup>10</sup> and cellobiulose<sup>11</sup> (IX), or 4-*O*-methyl-D-fructose<sup>12</sup> (X), are postulated to behave in a manner somewhat similar to that of the 3-*O*-derivatives of glucose. These derivatives in alkaline solution are believed to ionise (XI) and then undergo an electron transference eliminating the substituent group which is β to the carbonyl group. The dicarbonyl form (XIII) of the resulting enol (XII) finally undergoes a benzile

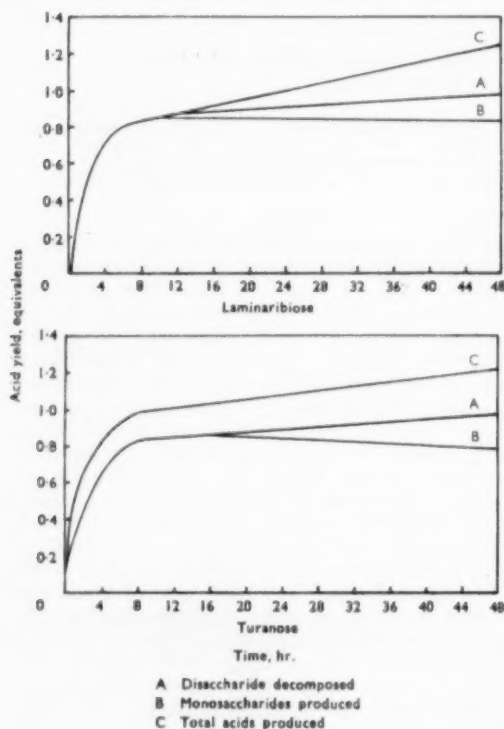


FIG. 1—The Degradation of Laminaribiose and Turanose by Saturated Lime-water at 25°C.

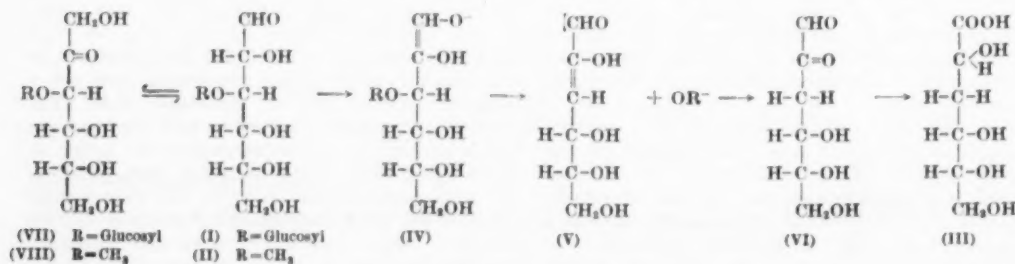


FIG. 2—The Alkaline Degradation of 3-*O*-Substituted Monosaccharides

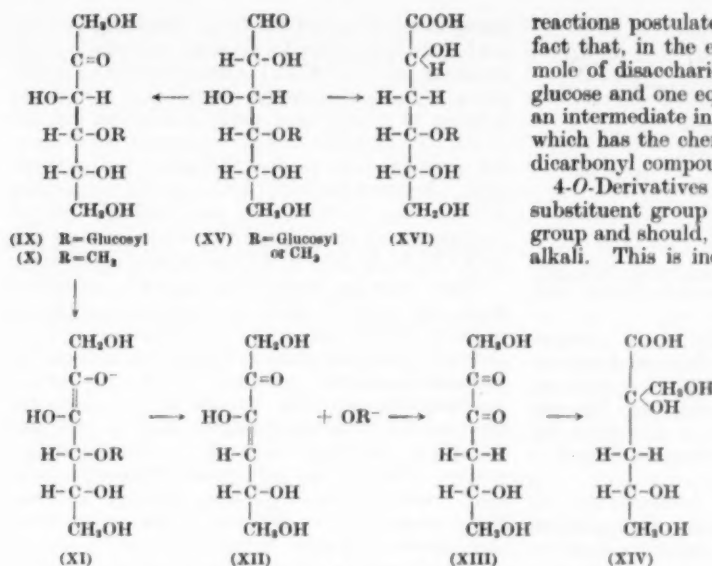


FIG. 3—The Alkaline Degradation of 4-O-Substituted Monosaccharides

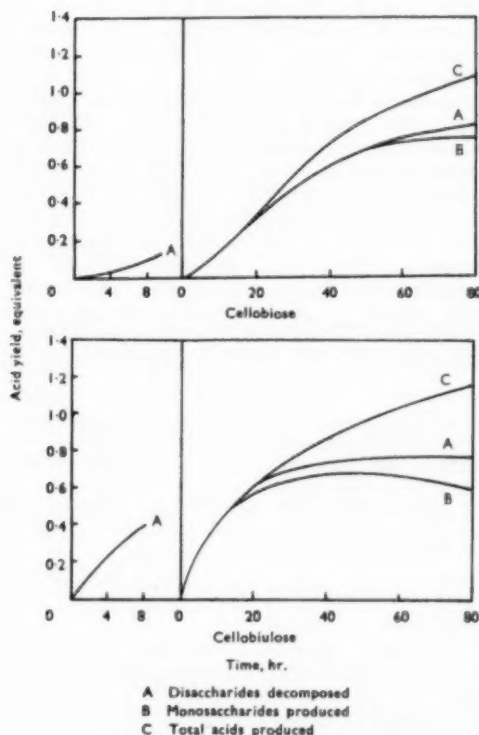


FIG. 4—The Degradation of Cellulose and Cellulose by Saturated Lime-water at 25°C.

acid rearrangement to give the acid (XIV). This acid, viz. isosaccharinic acid, is different from the one produced in the previous cases in that it is branched. The difference in structure is due to the different position of the substituent group which is eliminated. Evidence that the series of

reactions postulated is correct is provided by the fact that, in the early stages of the reaction, one mole of disaccharide decomposes into one mole of glucose and one equivalent of acid (Fig. 4). Also, an intermediate in the reaction has been isolated<sup>13</sup> which has the chemical properties expected of the dicarbonyl compound (XIII).

4-O-Derivatives of the aldoses (XV) have the substituent group in a  $\gamma$ -position to the carbonyl group and should, therefore, be relatively stable to alkali. This is indeed found to be the case, but

after a time lag of a few hours the aldoses are converted by a de Bruyn-van Ekenstein transformation into the corresponding ketoses, which then undergo degradation (Fig. 4). Elimination of the  $\text{C}_{(3)}$  hydroxyl group in the aldose derivatives could also occur, thereby producing a substituted metasaccharinic acid (XVI). However, substituted acids have not been

detected because, as in the similar cases of 3-O-substituted ketoses, the probability of such a reaction is small.

Degradation of the above compounds, and also of many others of various structures, illustrates the importance of an elimination of a substituent group which is in a  $\beta$ -position to a carbonyl group (a  $\beta$ -alkoxycarbonyl elimination). Such an elimination eventually leads to the formation of a saccharinic acid. It is therefore essential to consider examples where there is substitution at the hydroxyl group adjacent to the carbonyl group (Fig. 5), e.g. 2-O-D-xylopyranosyl-L-arabinose (XVII) and 2,3-di-O-methyl-D-glucose (XVIII). The former compound was found, as anticipated, to be relatively stable to lime-water at room temperature<sup>14</sup>, since a  $\beta$ -alkoxycarbonyl elimination would involve the production of a hydroxyl ion in an environment already containing hydroxyl ions. At elevated temperatures the disaccharide decomposes into acidic products by an unknown mechanism. The dimethyl ether of glucose is more reactive, and at room temperatures loses methanol<sup>15</sup> to give a product which has properties expected of XIX. Because of the presence of a methyl group at  $\text{C}_{(2)}$ , XIX cannot undergo the necessary rearrangements which lead to the formation of a saccharinic acid, and is therefore stable to alkali under mild conditions. From the latter case it is apparent that a substituent group adjacent to a carbonyl group does not prevent the occurrence of a  $\beta$ -alkoxycarbonyl elimination, an important fact when oxycelluloses are considered, but it does prevent further rearrangement of the molecule to an acidic product.

The reactions described above predominate in lime-water solutions of the sugars at room temperature. Somewhat more complex reactions occur in addition at elevated temperatures, as well as in

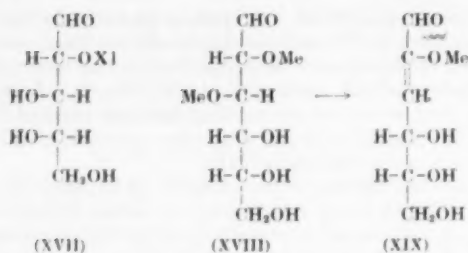


FIG. 5.—The Alkaline Degradation of Monosaccharide Derivatives containing a Substituent Group at an  $\alpha$ -Position to the Carbonyl Group

sodium hydroxide solutions. The nature of these additional reactions is not yet fully understood, but in sodium hydroxide solutions it is believed that the dicarbonyl intermediates, e.g. VI and XIII, are converted into acids of less than six carbon atoms as well as into saccharinic acids<sup>13</sup>.

#### OXIDISED MONOSACCHARIDE DERIVATIVES

It is now possible to consider the alkaline degradation of more complex molecules such as oxidised mono- and di-saccharides, and even oxidised polysaccharides. Most oxidising agents are non-specific in their action upon polysaccharides and give rise to a complex mixture of products in which the hydroxyl groups may have been oxidised to aldehydic, ketonic or carboxylic groups, and chain-scission even may have occurred. Periodic acid is one of the few specific oxidising agents, and only attacks glycol groups (Fig. 6). Thus methyl 4,6-*O*-benzylidene- $\alpha$ -D-glucoside (XX) is oxidised to a product (XXI) which undergoes a  $\beta$ -alkoxycarbonyl elimination in lime-water to give<sup>16</sup> 4-formyl-2-phenyl-2H-6H-1,3-dioxin (XXII) and a methyl hemiacetal of glyoxal (XXIII). The latter compound is unstable and gives methanol and glyoxal. Glyoxal too is unstable in alkaline solution, and undergoes an internal Cannizzaro reaction to give glycollic acid (XXIV). If the

benzylidene group of (XXI) is removed by mild acid hydrolysis prior to alkaline degradation, the resulting product (XXV) is then capable of undergoing a  $\beta$ -alkoxycarbonyl elimination in alkaline solution to give glyoxal methylhemiacetal and the enol (XXVI). The former compound reacts as in the previous case to give methanol and glycollic acid. Because the enol (XXVI) is not substituted at the C<sub>(2)</sub> position it can undergo further rearrangement through the dicarbonyl intermediate (XXVII) to  $\alpha$ , $\gamma$ -dihydroxybutyric acid (XXVIII).

These reactions explain the earlier observations made by Head<sup>17</sup> that the periodate-oxidation product (XXIX) of methyl  $\beta$ -D-glucoside did not yield glyoxal upon alkaline treatment, whereas the periodate-oxidation product (XXX) of methyl  $\beta$ -cellobioside did (Fig. 7). It is seen from the formulae for these two products that the glucoside derivative contains only an  $\alpha$ -alkoxycarbonyl system, whereas the cellobioside derivative contains both  $\alpha$ - and  $\beta$ -alkoxycarbonyl systems. Since under the conditions of the experiment, chain-scission would occur only in  $\beta$ -alkoxycarbonyl systems, glyoxal would only be produced from the cellobiose derivative.

More recently Theander<sup>18</sup> has separated the chromic-acid oxidation products of methyl  $\beta$ -D-glucoside. One such product, methyl 3-dehydro- $\beta$ -D-glucoside (XXXI) was found to be very sensitive to alkali, and in lime-water solution at 22°C., 90% was degraded in 20 min. An intermediate has been isolated and has been shown to undergo further reaction with alkali to give acidic products. Methyl 2-dehydro- $\beta$ -D-glucoside (XXXII) and 3-dehydro- $\alpha$ -D-glucoside degrade to give the same intermediate as methyl 3-dehydro- $\beta$ -D-glucoside. From the products isolated on reduction with Raney nickel, the intermediate would appear to be the dicarbonyl compound (XXXIII). The 2-dehydro-glucoside, apparently, is converted into the 3-dehydro-derivative by an

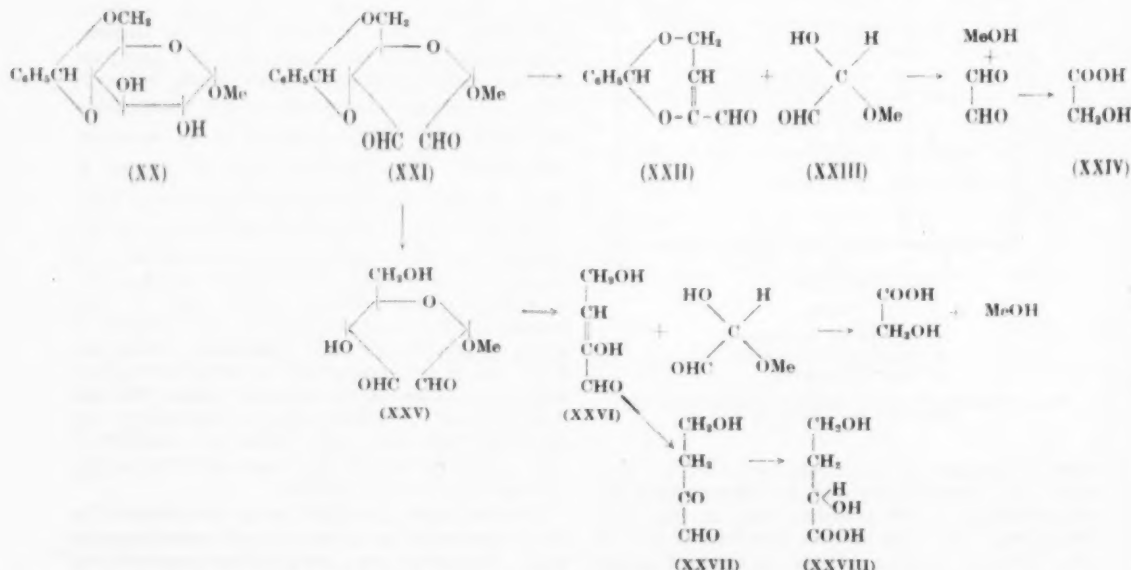


FIG. 6.—The Alkaline Degradation of Periodate-oxidised Methyl 4,6-*O*-Benzylidene- $\alpha$ -D-glucoside



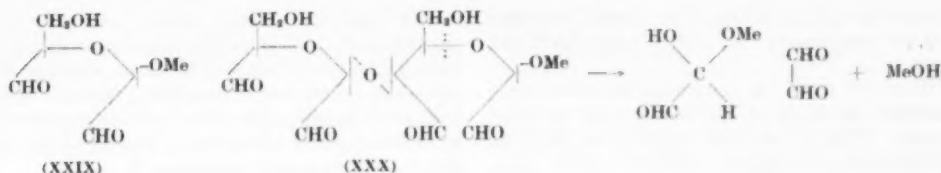
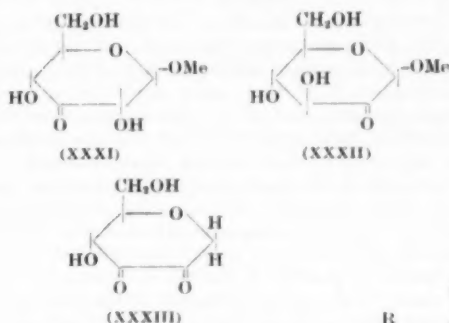


Fig. 7

isomerisation process analogous to the de Bruyn-van Ekenstein transformation, and then the latter undergoes a  $\beta$ -alkoxycarbonyl elimination to give the dicarbonyl compound (XXXIII). The dicarbonyl



compound is postulated to undergo a benzilic acid rearrangement to give a cyclic carboxylic acid, but the nature of the acidic product is of no importance in this discussion. The reaction of particular interest is the  $\beta$ -alkoxycarbonyl elimination which is responsible for the glycosidic chain-scission.

#### OXIDISED CELLULOSE

Because of the many aldehyde groups per molecule, periodate-oxidised cellulose is extremely sensitive to alkali. However, if the number of aldehyde groups is reduced by sodium borohydride reduction<sup>19</sup>, or by chlorous acid oxidation<sup>4, 20</sup>, the periodate-oxidised cellulose becomes less sensitive to alkali. It is not possible to eliminate completely the alkali-sensitivity by such treatments. This may be due to the fact that the

aldehyde groups form hemiacetals with the residual hydroxyl groups of the molecule, and may therefore become more resistant to oxidation or reduction. Two particular cases of the alkaline degradation of periodate-oxidised cellulose must be considered, viz. mildly and fully oxidised cellulose. In mildly oxidised cellulose the oxidised glucose repeating units are distributed evenly throughout a molecule, and may therefore be represented by (XXXIV), where R represents a glucose repeating unit. On treatment with alkali at room temperature such an oxidised cellulose will be expected to undergo a  $\beta$ -alkoxycarbonyl elimination causing chain-scission and the formation of the substituted enol (XXXV) and glyoxal which will rearrange to glycollic acid (Fig. 8).

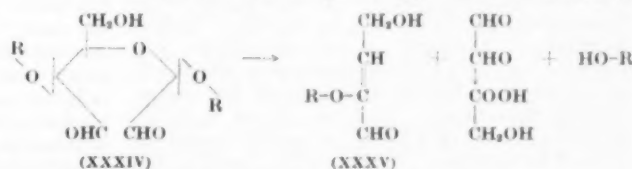


Fig. 8—Alkaline Degradation of Mildly Periodate-oxidised Cellulose

The products actually isolated<sup>21</sup> confirm these expectations, for the major acidic product was glycollic acid, with considerably less of  $\alpha$ -dihydroxybutyric acid. More fully periodate-oxidised cellulose (XXXVI) has many oxidised glucose units adjacent to each other. Treatment with alkali will then cause chain-scission by a  $\beta$ -alkoxycarbonyl elimination, giving rise to an enol substituted at C<sub>(2)</sub> (XXXVII). This enol is a hemiacetal of glyoxal, and therefore will rearrange into glyoxal and the free enol (XXXVIII), which will be converted into glycollic acid and  $\alpha$ -dihydroxybutyric acid respectively (Fig. 9). In

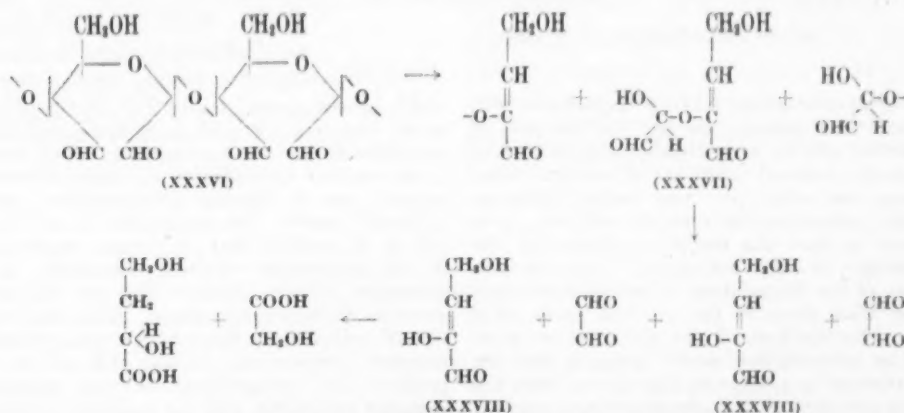


Fig. 9—Alkaline Degradation of Fully Periodate-oxidised Cellulose



this case the yields of the two acidic products should be comparable, and indeed this was found to be so.

Little recent work has been done on the alkaline degradation products of the non-specific oxidised celluloses. The hot alkaline degradation products of permanganate-oxidised cellulose have been shown to be a complex mixture of acidic products of 1-6 carbon atoms<sup>22</sup>. The nature of these products indicates that they did not arise from oxidised repeating units, but from a stepwise alkaline degradation of short-chain cellulose molecules arising from chain-scission at oxidised repeating units.

#### OLIGOSACCHARIDES AND POLYSACCHARIDES

A study of the alkaline degradation of disaccharides has indicated that if they have, or are capable of attaining by a de Bruyn-van Ekenstein transformation, a  $\beta$ -alkoxycarbonyl system, then they will degrade to an acid (arising from the reducing end) and a monosaccharide (from the non-reducing unit). Development of this would suggest that the reducing unit of a trisaccharide will split off as an acid, producing a new reactive site, viz. the reducing end of a disaccharide, which will then be capable of further degradation. Similarly, a tetrasaccharide will degrade to an acid and a trisaccharide, which will then degrade to further acid through the corresponding disaccharide. This was found to be so for cellotetraose (XXXIX), a partial hydrolysis product of cellulose. In lime-water solution the tetraose<sup>23</sup> was found to be converted by a de Bruyn-van Ekenstein transformation into the ketose cellotetraulose (XL) (cf. the similar case of cellobiose), which then degraded to cellotriose and an acid (isosaccharinic acid). The triose was then converted into the ketose derivative, cellotriulose (XLI), which was then degraded to cellobiose and further acid (Fig. 10).

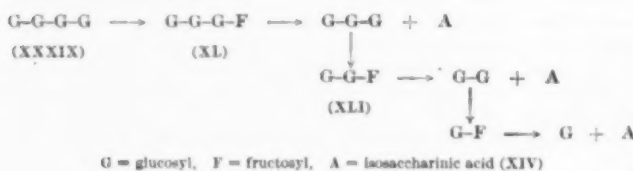


FIG. 10—Alkaline Degradation of Cellotetraose

This type of stepwise alkaline degradation will also occur with polysaccharides, but the rate of degradation will be considerably less because of the greatly reduced number of reactive sites (reducing end-units) per unit mass. With an insoluble polysaccharide such as cellulose, it is necessary to heat the reaction mixture for the degradation to be noticeable. The reaction products of the degradation of cellulose are more complex than those of the previous cases cited above. Identification of the major acidic component as isosaccharinic acid<sup>24</sup> indicates that the major reaction is a stepwise degradation from the reducing end through a  $\beta$ -alkoxycarbonyl elimination. However, identification of other acids, e.g.

formic, glycollic, lactic, acetic, and dihydroxybutyric acids, indicates that other reactions occur. The formation of some of these smaller acids, especially when a stronger alkali such as sodium hydroxide is used, may arise from the action of the hot alkali upon the dicarbonyl intermediate (XIII) in isosaccharinic acid formation<sup>27</sup>.

From the examples discussed above, cellulose itself would be expected to undergo a stepwise alkaline degradation from the reducing end until it is completely degraded. This is not so, for after a certain amount of degradation has occurred, the cellulose becomes resistant to alkali owing to the occurrence of a "stopping reaction"<sup>25</sup> and is not further degraded (Fig. 11). The group responsible for the alkali-resistance has been ascertained by the acid hydrolysis of alkali-stabilised cellulose and identification<sup>26</sup> of the major acidic product as metasaccharinic acid (III). The formation of this acid will be more apparent if the alkaline degradation of 4-O-substituted aldoses is reconsidered. In the discussion of these compounds, mention was made of the possibility of elimination of a hydroxyl group at C<sub>4</sub> to produce a substituted acid (XVI). Since the probability of such a reaction is small, it has not been possible to isolate such an acid. In the case of cellulose the presence of the acid group stabilises the molecule towards further attack by alkali, and therefore, since the degradation of cellulose involves the successive removal of many glucose units, the concentration of acid-terminated cellulose molecules will increase until it becomes of considerable importance.

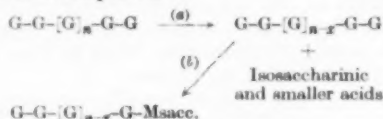


FIG. 11—Alkaline Degradation of Cellulose: (a) Stepwise Degradation, (b) "Stopping" Reaction

The effect of alkaline degradation upon the weight-average D.P. of cellulose is very small. This is because the degradation is stepwise from the reducing end of the molecules, and molecules of low D.P. will be preferentially extracted because of their greater solubility in alkali. At elevated temperatures (ca. 150°C. and above) a further reaction occurs<sup>27</sup>

which causes a rapid fall of D.P. of the cellulose, as in the case of acid hydrolysis, and also a considerable increase in weight-loss. This reaction is due neither to oxidation by residual traces of oxygen, nor to thermal decomposition, but to hydroxyl ions<sup>28</sup>. Its mechanism is not known, but it is certain that it causes chain-scission of the molecules, resulting eventually in the formation of new reactive sites for the normal stepwise degradation to occur. Thus the weight-loss of cellulose at these higher temperatures is inversely proportional to the D.P. of the final product (i.e. proportional to the number of reducing end-units), and the products of degradation are similar to those obtained at 100°C.

## CONCLUSIONS

A  $\beta$ -alkoxycarbonyl elimination reaction, which Isbell advanced to explain the alkaline degradation of unsubstituted monosaccharides, has been shown to be responsible for the degradation of model compounds of oxidised celluloses by lime-water at room temperature. At higher temperatures and with stronger alkalis, e.g. sodium hydroxide, more complex reactions occur. Some of the additional reactions may possibly be variations in mode of rearrangement of a dicarbonyl compound produced by a  $\beta$ -alkoxycarbonyl elimination. The products of alkaline degradation of several types of oxidised mono-, oligo-, and poly-saccharides indicate that chain-scission of the molecule may occur by a  $\beta$ -alkoxycarbonyl elimination reaction. However, reactions other than a  $\beta$ -alkoxycarbonyl elimination may also be responsible for chain-scission, but further study is necessary. The alkali-sensitivity of oxycelluloses may be almost completely eliminated by reduction of the reactive carbonyl groups, but at present this is not a commercial proposition.

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## References

- <sup>1</sup> Davidson, *J. Textile Inst.*, **29**, T 195 (1938).
- <sup>2</sup> Idem, *ibid.*, **25**, T 174 (1934).
- <sup>3</sup> Meller, *Tappi*, **36**, 366 (1953).
- <sup>4</sup> Idem, *ibid.*, **34**, 171 (1951).
- <sup>5</sup> For a more detailed discussion see W. M. Corbett in *Recent Advances in the Chemistry of Cellulose and Starch*, edited by J. Honeyman (London: Heywood, 1959) and the original papers quoted therein.
- <sup>6</sup> Corbett and Kenner, *J.C.S.*, 3274 (1954).
- <sup>7</sup> Kenner and Richards, *ibid.*, 278 (1954).
- <sup>8</sup> Isbell, *Bur. Stand. J. Res.*, **32**, 45 (1944).
- <sup>9</sup> de Bruyn and van Ekenstein, *Rec. Trav. chim.*, **19**, 1 (1900), and previous papers.
- <sup>10</sup> Corbett and Kenner, *J.C.S.*, 1789 (1954).
- <sup>11</sup> Idem, *ibid.*, 1431 (1955).
- <sup>12</sup> Kenner and Richards, *ibid.*, 1810 (1955).
- <sup>13</sup> Blears, Machell, and Richard, *Chem. and Ind.*, 1150 (1957).
- <sup>14</sup> Whistler and Corbett, *J. Amer. Chem. Soc.*, **77**, 3822 (1955).
- <sup>15</sup> Kenner and Richards, *J.C.S.*, 2421 (1956).
- <sup>16</sup> O'Meara and Richards, *ibid.*, 1204 (1958).
- <sup>17</sup> Head, *J. Textile Inst.*, **38**, T 389 (1947).
- <sup>18</sup> Theander, *Abstracts, XVth International Congress of Pure and Applied Chemistry—Organic Chemistry Division* (Paris: 1957), p. 44.
- <sup>19</sup> Meller, *Chem. and Ind.*, 1204 (1953).
- <sup>20</sup> Rutherford, Minor, Martin, and Harris, *Bur. Stand. J. Res.*, **29**, 131 (1942).
- <sup>21</sup> O'Meara and Richards, *J.C.S.*, 4504 (1958).
- <sup>22</sup> van Faber and Tollens, *Ber.*, **32**, 2595 (1899); Godman, Haworth, and Peat, *J.C.S.*, 1909 (1939).
- <sup>23</sup> Corbett and Kenner, *ibid.*, 1431 (1955).
- <sup>24</sup> Murumow, Sack, and Tollens, *Ber.*, **34**, 1427 (1901); Green, *Tappi*, **39**, 472 (1956); Richards and Sephton, *J.C.S.*, 827 (1957).
- <sup>25</sup> Richtzenhain and Abrahamsson, *Scensk Papperstidning*, **57**, 538 (1954); Samuelson and Wennerblom, *ibid.*, **57**, 827 (1954).
- <sup>26</sup> Machell and Richards, *J.C.S.*, 4500 (1957).
- <sup>27</sup> Samuelson, Grangard, Johnson, and Schramm, *Scensk Papperstidning*, **56**, 779 (1953).
- <sup>28</sup> Corbett and Richards, *ibid.*, **60**, 791 (1957).

## Discussion

Mr. J. A. CLARKE: The degradation of linen is assessed by measuring the alkali-solubility of the fibre under standard conditions (10N. NaOH at room temperature for a standard time, then diluting to 2N.; the fibre previously being scoured in mild alkali). Does the lecturer consider that this test is suitable for the control of bleaching processes?

Dr. CORBETT: The method referred to is based upon the extensively used method for determining the  $\alpha$ -cellulose content of wood pulp, etc. It measures the impurities (i.e. the material soluble in strong alkali) in the sample, and is a valid test for the control of linen bleaching as far as purity of the final product is concerned. However, it gives little indication of the extent of oxidation of the cellulose by the bleaching agent, for any oxidised cellulose molecule on treatment with the strong alkali will undergo degradation to smaller molecules which will probably be dissolved by the alkali. The method does not differentiate between extracted material arising from the original impurities in the linen and that arising from oxidised cellulose molecules.

Mr. T. C. MASON: In the reaction which involves breaking off glucose units from cellulose, does the presence of stronger alkali encourage or inhibit the reaction, i.e. does the stronger alkali cause the stable molecule to be achieved more quickly?

Dr. CORBETT: The weight-loss resulting from the sodium hydroxide degradation of cellulose increases with an increase in alkali concentration. The increase may possibly be due to the more concentrated alkali inhibiting the "stopping reaction", but is more likely due to an increase in solubility of the fragments in stronger alkali. An interesting effect is observed if the cellulose is pretreated in the cold with concentrated alkali and the alkali diluted to a fixed normality before degradation is carried out in the hot solution. This procedure causes a decrease in weight-loss, particularly if alkali of swelling strength is used for the pretreatment (see G. Machell and G. N. Richards, *Tappi*, **41**, 12 (1958); W. M. Corbett and J. Kidd, *ibid.*, **41**, 137 (1958)).

## COMMUNICATIONS

# The Separation and Identification of Commercial Dyes by Paper Chromatography

## I—Acid Dyes

C. McNEIL

The use of paper chromatography in separating commercial dyes is discussed briefly and some simple apparatus is illustrated. Methods are given for the separation of level-dyeing, milling acid and neutral-dyeing acid dyes, as well as chrome dyes. Possible applications are outlined.

## INTRODUCTION

The use of paper chromatography for the separation of otherwise inseparable mixtures is now very common. The technique has been applied to almost every known type of chemical compound and many text-books and publications describing its uses and applications are available.

Information as to its use in the separation of commercial dyes is, however, relatively scanty<sup>1-3</sup>. This may be due to the fact that dyes belonging to the same dyeing class may be chemically quite different, so that a solvent or eluent which will separate one mixture is often totally ineffective for a different mixture.

It is, however, possible to avoid this difficulty by using a graded series of solvents, and the present paper deals with a general method for separating acid dyes of the various types, as well as after-chrome dyes. It is hoped eventually to publish information relating to other classes of dyes.

## METHODS IN GENERAL USE

The methods commonly used for paper chromatographic separations are—

- (1) Circular paper methods
- (2) Ascending paper methods
- (3) Descending paper methods
- (4) Two-dimensional methods
- (5) Paper electrophoresis, which may or may not be continuous.

Since the present paper is intended to be useful in ordinary dye-house laboratories, only the simplest apparatus has been used, and only the first three methods will be discussed, although excellent separations can be obtained by two-dimensional and electrophoresis methods.

## Circular Paper Method

The simplest method is to use ordinary 11-cm. circles of Whatman No. 1 filter paper. The dye mixture is dissolved in 2% ammonium hydroxide, and a small drop of this solution is applied at the centre of the filter paper and the spot allowed to dry. Two parallel cuts about  $\frac{1}{4}$  in. apart are then made from the outside edge of the paper into the coloured spot, so that, on folding down, a  $\frac{1}{4}$  in. paper wick is formed. For holding the paper, two circular glass plates of slightly greater diameter than the paper are used, one having a hole, just large enough to allow the wick to pass through, drilled through its centre. The wick is inserted through this hole, and the paper covered with the

other glass plate, so that it is sandwiched between the two plates. The wick is next inserted into a Petri dish containing solvent, with the glass plates and paper resting on top (Fig. 1). The apparatus is then left until a satisfactory separation is obtained. Many other circular plate methods, using larger papers, are available, the apparatus being obtainable from firms specialising in chromatographic equipment. However, for the experiments reported in this paper, the apparatus described above—which can be made in any laboratory—was quite adequate.

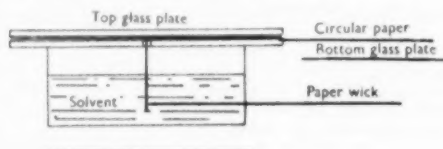


FIG. 1—Circular Paper Method

## Ascending Paper Method

Any convenient tank, jar or tube which can be made leak-proof may be used, whilst commercially available equipment ranges from small tubes to tanks capable of taking large paper sheets.

In the experiments described in this paper ordinary gas-jars were used. A small glass hook was made by pulling out and bending glass rod, and this was inserted through the rubber stopper used to close the open end of the glass jar. Sufficient solvent was poured in to cover the bottom to a depth of 1 cm., the stopper was inserted, and the jar allowed to stand until the atmosphere inside was saturated. A strip of

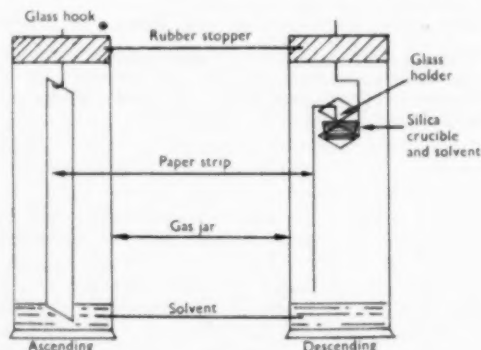


FIG. 2—Paper Strip Method

Whatman No. 1 or Whatman No. 3 chromatographic paper measuring 22 cm.  $\times$  2½ cm. was cut, and the dye mixture (again dissolved in 2% ammonium hydroxide) was spotted on the paper 2 cm. from the end of the strip. The paper was then impaled on the hook at a point 2 cm. from the other end of the strip, and inserted into the jar, so that the lower edge was just below the surface of the solvent, care being taken to ensure that the paper was hanging vertically without touching the walls of the jar (Fig. 2). The apparatus was then left until a clear separation was obtained.

#### Descending Paper Method

This is a very common method, the paper being suspended in a closed vessel so that it hangs freely, with its upper end dipping into a reservoir containing the solvent. A drop of the mixture is applied near the upper end of the paper, so the solvent front passes over the dye spot, and separation takes place in a downward direction.

Tanks and troughs are commercially available in various sizes, but simple apparatus is easily made.

The apparatus used by the author consists of a gas-jar fitted with a rubber stopper through which is inserted a glass holder which supports a silica crucible. The holder is easily made by bending glass rod as shown (Fig. 3). Some of the solvent is poured into the jar, which is then left until the atmosphere inside is saturated.

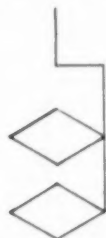


Fig. 3—Glass Holder

The silica crucible is then filled with solvent and inserted in the holder. A strip of either Whatman No. 1 or No. 3 paper is cut and bent over so that it dips into the crucible, passes over the top glass rod to prevent syphoning, and then hangs vertically without touching the sides of the jar. The dye solution is spotted on to the paper below the holder and the apparatus left until a separation is obtained.

#### SEPARATION OF ACID DYES

The partial separation of level-dyeing acid dyes has been described by Midgellow<sup>4</sup>. In most cases, however, this method gives broad diffuse bands which merge into each other without giving clear separations, and it is not effective with most neutral-dyeing or milling acid dyes, or with chrome dyes. In order to make the method applicable to all classes of acid dyes and chrome dyes, it is necessary to select one of a series of solvents, and the following series (Table I) has been evolved after considerable experiment. One or other of these solvents will give satisfactory separations

with the great majority of mixtures, i.e. although mixtures of acid dyes or chrome dyes may be encountered in which the  $R_f$  values are so close together as to defy separation by one solvent, it is extremely unlikely that this will apply to all seven solvents.

TABLE I  
Composition (ml.) of Solvents used for Chromatographic Separations

No.	n-Butanol	Commercial Ethyl Alcohol	Ammonium Hydroxide (2%)*†
1	100	—	20
2	90	10	29
3	80	20	45
4	60	40	178
5	4	6	40
6	4	6	90
7	—	—	100

\* 2 ml. of 0.880 ammonia plus 98 ml. of distilled water.

† The amounts of 2% ammonium hydroxide used are just sufficient to saturate the butanol or butanol-ethanol mixtures in solvents 1, 2, 3, and 4.

#### Procedure

About 0.25 g. of the mixture to be separated is dissolved in a little (ca. 25 ml.) of the 2% ammonium hydroxide solvent, and simultaneous trials using all seven solvents are made by the circular paper method previously described, using Whatman No. 1 filter paper circles. After allowing the separations to continue for about 2 hr., it is obvious which solvent is the most effective, and this is chosen for a complete separation, using either the ascending or the descending paper-strip method. The best separations were obtained on the ascending strip using Whatman No. 3 paper, and on the descending strip using Whatman No. 1 paper.

The following mixtures of commercial dyes were found to give excellent separations—

- A Erio Fast Cyanine S (C.I. Acid Blue 45)  
Erio Fast Cyanine Green GS (C.I. Acid Green 25)  
Erio Fast Red BS (C.I. Acid Red 61)
- B Cyanine Fast Yellow M (C.I. Acid Yellow 42)  
Cyanine Fast Scarlet G (C.I. Acid Red 97)  
Orange II (C.I. Acid Orange 7)
- C Coomassie Ultra Sky SES (C.I. Acid Blue 112)  
Coomassie Yellow 6GS (C.I. Direct Yellow 8)  
Coomassie Red BRS (ICI)
- D Carbolan Brilliant Green 5GS (C.I. Acid Green 28)  
Carbolan Yellow 3GS (C.I. Acid Yellow 72)  
Carbolan Crimson BS (C.I. Acid Red 138)
- E Polar Brilliant Blue RAW (C.I. Acid Blue 80)  
Polar Orange R conc. (C.I. Acid Orange 45)  
Polar Brilliant Red BN conc. (C.I. Acid Red 130)
- F Coomassie Fast Orange G150 (C.I. Acid Orange 33)  
Coomassie Violet 2RS (C.I. Acid Violet 9)  
Solway Sky Blue BS (C.I. Acid Blue 78)
- G Solochrome Orange GRS (C.I. Mordant Orange 6)  
Solochrome Red ERS (C.I. Mordant Red 7)  
Solochrome Green V 150 (C.I. Mordant Green 15)
- H Superlan Rubinol R (C.I. Acid Red 80)  
Alizarin Brilliant Green 5G (C.I. Acid Green 41)  
Merantine Blue 5G (LBH)



- I Brilliant Alizarin Milling Blue 2RL  
(C.I. Acid Blue 126)  
Brilliant Alizarin Milling Red FBL  
(C.I. Acid Red 143)  
Brilliant Alizarin Milling Violet FBL  
(C.I. Acid Violet 48)

The  $R_f$  values of the individual dyes in these mixtures are given in Table II. They were obtained by means of the circular paper method, using Whatman No. 1 paper, and are given in order to illustrate the use of this method.

The  $R_f$  values in Table II are not very accurate, owing to the small size of the paper circle and the irregularities in flow characteristics of the paper. The values will also vary with conditions, different types of apparatus and different papers, and will be different from those obtained by ascending or descending methods. They are given only to illustrate the kind of separation which can be expected. When using the method,  $R_f$  values should be standardised by the operator under his own conditions.

It has been found that, if a dye separates as a clear sharp band in the circular paper method or as a spot without pronounced "tailing" in the strip methods, the  $R_f$  values are constant under the same conditions. If, however, a dye separates as a broad diffuse band or shows marked "tailing", the  $R_f$  value will vary considerably with the concentration of the dye on the paper.

It is possible to modify the method by using two or more of the solvents in turn. Thus the original trial may show that in one solvent the  $R_f$  value of a component *A* is very much higher than the others, whilst in another solvent component *B* has a very much higher  $R_f$  value than the others. By using the descending strip method and the first solvent, it is possible to allow component *A* to separate completely to the end of the strip. The strip can then be dried and the part containing *A* cut out. It is then returned to the jar, and, using the second solvent, component *B* will separate. In this way each component may be separated in turn. The same technique may be applied if two-dimensional apparatus is available.

TABLE II  
 $R_f$  Values at 19–20°C. in Solvents 1–7

Dye	Solvent No.						
	1	2	3	4	5	6	7
Erio Fast Cyanine S*	(a) 0	0	0	0	0	0.04	0.02
	(b) 0.05	0.05	0.12	0.09–0.24	0.29–0.38	0.73	0.54–0.70
Erio Fast Cyanine Green GS	0.35	0.40	0.41	0.54	0.59	0.88	0.92
Erio Fast Red BS	0.16	0.27	0.29	0.48	0.49–0.56	0.79	0.84
Cyanine Fast Yellow M	0.44	0.57	0.58	0.66	0.90	0.90	0.88
Cyanine Fast Scarlet G	0.50	0.62	0.67	0.66	0.85	0.74	0.08–0.36
Orange II	0.47	0.59	0.61	0.66	0.85	0.67	0.66
Coomassie Ultra Sky SES	0.35	0.47	0.53	0.60	1.0	0.90	0.81
Coomassie Yellow 6GS	0.43–0.62	0.56	0.63	0.65	0.0–0.37	0.0–0.15	0.0–0.15
Coomassie Red BRS**	(a) 0.35	0.47	0.50	0.57	0.8	0.63	< 0.05
	(b) —	—	—	—	0.87	0.71	—
Carbolan Brilliant Green 5GS	0.52	0.54	0.62	0.72	0.94	0.41–0.64	< 0.05
Carbolan Yellow 3GS	0.93	0.92	0.92	0.95	0.92	0.0–0.18	< 0.05
Carbolan Crimson BS	0.37	0.41	0.54	0.61	0.95	0.18–0.41	< 0.05
Coomassie Fast Orange G***	(a) 0.19	0.32	0.54	0.61	0.91	0.82	0.78
	(b) 0.38	0.45	0.62	0.61	0.91	0.82	0.78
Coomassie Violet 2RS†	(a) 0.28	0.39	0.60	0.60	0.94	0.93	0.86
	(b) 0.50	0.58	0.71	0.71	0.94	0.87	0.50
Solway Sky Blue BS	0.53	0.66	0.71	0.71	0.73	0.62	0.32–0.44
Solochrome Orange GRS	0.45	0.42	0.50	0.57	0.55	0.26	0.13
Solochrome Red ERS	0.35	0.39	0.47	0.51	0.67	0.26	0.13
Solochrome Green V	0.51	0.50	0.59	0.62	0.0–0.38	0.0–0.14	0.0–0.09
Superlan Rubinol R	0.51	0.51	0.57	0.64	0.84	0.34–0.70	0.52
Alizarin Brilliant Green 5G	0.39	0.43	0.54	0.60	0.84	0.78	0.48
Merantine Blue 5G	0.73	0.71	0.78	0.80	0.89	0.0–0.34	0.0–0.28
Brilliant Alizarin Milling Blue 2RL	0.97	0.96	0.94	0.97	0.40–0.80	0	0
Brilliant Alizarin Milling Red FBL‡	(a) 0.30	0.33	0.31	0.61	—	—	—
	(b) 0.43	0.46	0.56	0.61	0.94	0.83	0.66–0.77
	(c) 0.91	0.83	0.81	0.81	—	—	—
Brilliant Alizarin Milling Violet FBL†	(a) 0.15	0.20	0.75	0.68	0.97	0.58–0.73	0.1–0.42
	(b) 0.79	0.70	—	—	—	—	—
Polar Brilliant Blue RAW	0.46	0.53	0.58	0.64	1.0	0.93	0.44–0.59
Polar Orange R§	(a) 0.40	0.50	0.53	0.54	0.0–0.69	0.0–0.37	0.0–0.22
	(b) 0.08	0.15	0.13–0.31	0.18–0.36	—	0.82	0.33
Polar Brilliant Red BN	0.34	0.44	0.53	0.54	0.87	0.70	0.39

\* Component (a) was a blue direct dye

\*\* Two distinct red dyes, (a) yellower than (b)

\*\*\* Two distinct orange dyes

† Two distinct violet dyes

‡ Three distinct red dyes

§ (a) Yellow-orange, (b) red-orange



## APPLICATIONS

As is seen from the  $R_f$  values given in Table II, many commercial dyes are mixtures. This does not necessarily reflect the deliberate policy of the dye manufacturer, but is usually due to the presence of closely related isomers, or to different degrees of sulphonation or different positions of the sulphonic group. The detection of isomers, as well as the isolation of the components of deliberate mixtures, can be achieved by means of paper chromatography, even if only very small quantities of dye are available. The  $R_f$  values of the dyes in these solvents are reasonably constant under the same temperature conditions, except in the cases previously mentioned, and this fact can be used, in suitable cases, to identify the components of mixtures. It is also possible to dry the paper, cut out the separated spots and apply the usual tests with acids, alkalis, etc.; the results are then compared with those of the same tests carried out on the suspected dye spotted on similar paper. All acid dyes are removable from the paper by boiling with the 2% ammonium hydroxide, so if a spectrophotometer is available, the characteristic absorption curve of the dye can be determined.

One objective is to be able to take a dyed

pattern, strip off the dyes, separate them, and then identify the components. At present this can be done with wool patterns dyed with level-dyeing acid dyes, but not with patterns dyed with milling acid or neutral-dyeing acid dyes, or with chrome dyes. Level-dyeing acid dyes on wool can be stripped more or less completely by boiling dilute ammonium hydroxide, the solution concentrated and the components separated and identified as described; but with the other classes no reagent has yet been found which will give adequate and even stripping of mixtures dyed on wool without destroying the dyes, or at least largely altering the colour and the  $R_f$  value. It is hoped, however, that a suitable stripping agent will eventually be found which will enable the method to be extended to all classes of acid dyes and chrome dyes on wool.

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## References

- <sup>1</sup> Cropper, F. R., *J.S.D.C.*, **61**, 162 (1945).
- <sup>2</sup> Klingsberg, E., *ibid.*, **70**, 563 (1954).
- <sup>3</sup> Elliott, K., and Tolosz, L. A., *ibid.*, **73**, 8 (1957).
- <sup>4</sup> Midgellow, G. W., *Hexagon Digest*, (3), 3 (July 1948).

## The Origins of English Calico Printing

(The late) P. C. FLOOD

The generally accepted theory that the first English calico printworks was established at Richmond, Surrey, in 1690 is considered to have no basis in fact. From examination of new evidence, it is concluded that the industry was established in 1676, probably by William Sherwin at West Ham, and for the next twenty-five years was confined to areas in East London, on both sides of the River Lea, at Bow and West Ham. By this time (1676) the English printers had mastered the secrets of mordant printing with madder, having eventually solved the problems of thickeners and the clearing of the ground.

In 1955 I was fortunate enough to discover a large number of fully documented eighteenth and early nineteenth century English textile-printers' pattern-books. They were first publicly shown in an exhibition organised by the Victoria and Albert Museum at the Cotton Board Design Centre in Manchester in the winter of 1955-6, in which an attempt was made for the first time to plot the stylistic changes in English printed textiles almost from year to year from the mid-eighteenth century down to the present day<sup>1</sup>. During a visit to the United States during 1958<sup>2</sup> it became clear that quite unsuspected quantities of early English printed textiles had been preserved in American public and private collections—their dates often misunderstood, and their English origins forgotten. This rich additional evidence has made it possible to plan a much enlarged version of the Manchester exhibition, to be held in London at the Victoria and Albert Museum during the summer of 1960.

Examination of these pattern-books and textiles has prompted a reassessment of the evidence concerning the origins of English textile printing, and the techniques used by the eighteenth and early nineteenth century printers. The conclusions which have so far been reached will be set out in this series of articles. It will be found that at many points they differ considerably from the facts as

hitherto normally accepted. In particular they will show that on many controversial issues the only direct evidence of the achievements of the early English printers is to be found in foreign references which have been completely ignored by English writers.

It must be confessed that there are still many gaps and puzzling inconsistencies in the story, some of which may well be due to a layman's misunderstanding of technical details—both chemical and mechanical. Nevertheless it is hoped that the publication of even tentative conclusions will help towards their ultimate clarification.

Everyone agrees that in England, as in all the other Western European countries, the origins of the modern textile-printing industry must be traced back to the end of the seventeenth century. Before that, textile printing was limited to coarse linens and canvas wall-hangings printed with oil stains. The change was, of course, the direct result of the immense popularity of the brilliant fast-coloured Indian chintzes, which were imported by the East India Companies in increasing quantities from the early seventeenth century onwards. They provided a direct incentive to the production of satisfactory substitutes at home and ultimately gave birth to European calico printing. So much is, in general, agreed; but there is immediate uncertainty if more specific questions

are raised. Exactly when, where and by whom was calico printing first practised in England? Was this earlier or later than in France, Holland, Germany or Switzerland? What techniques were used by these pioneers, and in particular had they discovered the "secrets" of the Indian chintz producers, and, if so, how? A special investigation<sup>3</sup> was set on foot last year to get to the bottom of these questions. As a result, some can now be answered definitely, others remain obscure, and in the process some well-established legends have been exposed.

Almost all writers have hitherto agreed in stating that the first English calico-printworks was established in Richmond, Surrey, in 1690. This fact was first given wide currency by Edward Baines, in his admirable *History of the Cotton Manufacture* (London 1835)<sup>4</sup>, and has ever since been simply repeated without any checking of original sources. Baines, however, was merely repeating a passing reference made only two years earlier by James Thomson of Clitheroe, the leading calico printer of his generation. This occurred during his (presumably extempore) evidence before a Select Committee on Manufactures, Commerce and Shipping. In answering a general question he stated that "the origin [of English calico printing] dates from about the year 1690, when a small printground was established on the banks of the Thames, at Richmond, by a Frenchman, who in all probability was a refugee after the revocation of the edict of Nantz (*sic*)"<sup>5</sup>. In this oral statement Thomson provides no supporting evidence; he never repeated it in any of the numerous pamphlets which he later wrote about calico printing; and some details about early eighteenth century developments which he gave in the second part of the same answer are certainly inaccurate.

Despite these difficulties, Thomson's statement has not merely been regularly repeated since, but has been frequently embroidered by the addition of picturesque but totally unrelated details. For example, in an article in the *English Historical Review* on "The Beginnings of Calico-printing in England"<sup>6</sup>, it is categorically asserted that Thomson's Frenchman was a certain René Grillet (though now transformed from a Protestant refugee to a Roman Catholic!) who took out a patent for calico printing in this same year 1690. However, according to the Patent Office records, no English patent has ever been granted to anyone of that name, and no calico printing patent was granted in 1690<sup>7</sup>. Moreover there is no shred of evidence to associate Grillet with Richmond. Despite this the same article specifies the exact location of the printfield very precisely—in the Old Deer Park, fifty yards from the Thames—and tells us that "a great number of men and women were employed in this factory, and they were 'a saucy and independent lot' ". This all reads most satisfactorily until we trace this last phrase back to its source<sup>8</sup>, and find that it was originally used in reference to some printers in Richmond in about 1760, and has not the slightest relevance to any seventeenth century conditions.

The only English book on the history of calico

printing makes an even more peculiar mistake. It identifies the Richmond pioneer as "Jacques Deluye, a Swiss"<sup>9</sup>. This was almost certainly copied—or rather miscopied—from an article published in this *Journal* in 1903 by John Stirling, which gave the name as Jacques Deluze<sup>10</sup>. It is true that there was a printer of this name, but he was a Frenchman who moved not to Richmond, but to near Neuchâtel, Switzerland, in 1691, and later set up one of the earliest Swiss printworks. His whole career is well attested by Swiss references<sup>11</sup>. They imply that he passed through Holland on his way from France to Switzerland, but I can trace no justification whatever for linking him with England.

Equally misleading is the statement that the man's name "is generally given as Cabannes", which has unfortunately been given wide currency in a Victoria and Albert Museum publication<sup>12</sup>. In fact the name has only once been given as Cabannes, and that as a result of an obvious slip in one of the numerous publications by Henri Clouzot, the French authority<sup>13</sup>. He must have muddled up his notes and confused an English pioneer in France with a French pioneer in England, for only four pages later he correctly sets out the well-established details of how Cabannes (always said to be English despite his name) set up a printworks in the Arsenal at Paris in 1754. We remain, therefore, as far as ever, both in time and place, from Thomson's mysterious refugee.

Unfortunately last year's search for original documents produced less positive evidence to replace these confusions than had been hoped. It did, however, become clear that the cradle of English calico printing is to be sought in East London and on both sides of the River Lea at Bow and West Ham, and that Surrey did not become a regular centre of the industry until a full generation later.

The beginning of the search was naturally the fifty names of printers appended to the petition presented to the House of Lords in 1696<sup>14</sup> at a time when the silk and wool interests were campaigning for a prohibition of cotton chintzes—whether imported from India or printed at home. The names are as follows—

Wm. Sherwin	Joseph Bundy
John Spanier	Will. Hamand
Benjamin Naylor	David Pechell
Harmon Markillum	Partellemy Gautie(r)
John Hopkins	Robert Smith
Louis Roffiere	John Morris
John Edwards	John Taylor
John Line	John Ley
Edward Allin	Rich: Langly
James Merrick	Chris: Needle
John Coleman	Charles Hunt
Job Brocas	John Briggs
John Mark	Samll Burroughs
George Powell	John Yeasley
Richard Payne	George Briggs
James Watson	D. Richards
Chs: Hill	Nicholas Dean
Henry Ayseough	Pr. Mauvillain
Richard Lewis	Tho: Steed
James Parbery	Tho: Gibbons
John Woodfield	Joseph Hull
Henry Harding	John Hutton
Richard Boyfield	John Panbery
Joseph Mobs	J. Dumbleton
Joseph Dumbleton	William Lewis

Unfortunately the petition records neither the place of work of the signatories nor the size of their establishments, although William Sherwin, who headed it, is reported as having stated in evidence before the House of Lords<sup>15</sup> that "my next neighbour and myself employ about 400" (whether each or together is not clear). Examination of parish registers and similar records has so far disclosed the place of work of only six out of the fifty petitioners, of whom five operated in East London or on the River Lea (Sherwin himself at West Ham, and the others at Hackney, Stepney, Spitalfields and Bow). In addition eleven further printers, who did not sign the petition, have been traced before 1700, of whom one operated in West Ham and the other ten in East London (Stepney, Bow and Poplar).

By contrast with this concentration in East London and along the River Lea, no printers can be traced anywhere in Surrey—or indeed anywhere south of the Thames—during the seventeenth century<sup>16</sup>. One appears in Lambeth in 1702, and another in Wandsworth in 1707, but it is not until after 1715 that the number of works begins to increase or to spread up the River Wandle to Wimbledon and Tooting. The earliest evidence for Richmond does not appear until the 1740's, and then rests on nothing more reliable than a passing reference in Horace Walpole's *Anecdotes of Painting in England*<sup>17</sup>.

It is surprising to find that quite a number of these early East London printers were at addresses some distance from any water—such as Bunhill Fields or Moorfields. This can only be explained in terms of a distinction which was made very clearly by contemporary commentators between *master-printers* and *job-printers*. For example, David Martin, in the report which he presented to the Board of Trade and Plantations in 1719 on behalf of the Weavers' Company in their campaign for the prohibition of calico printing<sup>18</sup>, listed twenty-six master-printers, but added that there were also "eighty jobb-printers". He described them as being "those that print old calicoes and linnens, which gives a great encouragement to servants to Robb their Masters or Mistresses, for by getting it printed, alters it so much, as it cannot be known again". More tangible evidence of their existence is provided by the trade-card of Jacob Stampe, in the Bagford Collection at the British Museum<sup>19</sup>. Although the card is not dated, it is thought to date from before 1700. It advertises printing on "all sorts of Calicoes . . . New or Ould". The address at Houndsditch, some way from the river, clearly marks Stampe as a job-printer, and points the distinction between the properly established master-printers such as William Sherwin, with considerable factories on the Rivers Thames, Lea or Wandle, and the small job-printers who could manage with primitive methods not requiring great quantities of water. If, according to Martin's report, the proportion of the former to the latter was twenty-six to eighty in 1719, we should probably be right in assuming that of the fifty who signed the petition in 1696, the majority—and certainly all those with

addresses away from the rivers—were small job-printers, and only a dozen at the most were master-printers on the Thames or Lea.

Having thus replaced Richmond by East London, it would be satisfactory if we could similarly replace Thomson's date of 1690 with something better based. Unfortunately we cannot. On the one hand we can argue that the proper date must be considerably earlier than 1690, if only because it is inconceivable that by 1696 there could already have been over fifty separate establishments employing several hundred men, if the first works had been started only six years previously. On the other hand, as soon as we attempt to push the date backwards, we come up against the fact that there is a total absence of any tangible evidence for a date earlier than 1696. Not one single reference to a calico printer as such has so far been traced in any London parish-register or other official document before 1696.

Only one explanation for this contradiction can be found. In 1676 William Sherwin was granted a patent (No. 190) "for a new way for printing broad callicoe". Experience shows that it would be unwise to draw any conclusions from an early patent such as this, if it stood alone, especially when, as with Sherwin's, the actual specification has not survived. However, we know that by 1696 Sherwin was the acknowledged leader of the industry, and we can hardly doubt, therefore, that he owed this position to his patent. The term of the patent was for fourteen years, expiring in 1690. It therefore seems reasonable to suggest that between 1676 and 1690 Sherwin exercised a virtual monopoly, so that no other calico printers are to be found in the registers; but that within a few years after 1690 enough competitors had entered the field to bring the budding industry to the point which we know it to have reached in 1696.

If this assumption is correct, then we are justified in regarding 1676 as the proper date for the origin of English calico printing, which would place it two years earlier than the foundation of the Amersfoort factory outside Amsterdam, which is usually accepted as the beginning of the industry in Holland<sup>20</sup>. Certainly we have the support here of the earliest of all English commentators, namely, Adam Anderson. In his forty years' service as Clerk of the South Sea Office he would have had access to the records of the Sherwin patent, and there can be no doubt that he had it in mind when he wrote, in his *Origin of Commerce* (1764)<sup>21</sup> that "it was in or about the Year 1676, that the printing of Calicoes was first set on Foot in London".

Two other scraps of evidence, from the records of the East India Company and the Royal African Company respectively, have sometimes been quoted as relevant to the origins of English textile printing. The first is a letter sent to India by the London office of the E.I.C. as early as February 1669. G. P. Baker, in his pioneer work on Indian chintzes<sup>22</sup>, first published this letter and quoted it as saying that there had arisen in England a "great practice of painting large branches for hangings of roomes", which it would be sensible for the Indians to copy. John Irwin, of the India



Section of the Victoria and Albert Museum, is positive, however, from a recent inspection of the original letter, that the correct reading should be "printing large branches for hangings of roomes". It could well be claimed, therefore, as the earliest known reference to calico printing in England. The date is, however, so unexpectedly early and unsupported by any other evidence, that one is tempted to explain it as being either a clerk's slip of the pen, or else a reference to canvas, or even paper, wall-hangings block-printed in oil-stains.

A strong argument for doubting its relevance to calico printing is the fact that at precisely the same date as this E.I.C. letter, the leading chemists in England—led by Robert Boyle and Robert Hooke—were proudly presenting at various meetings of the Royal Society, for the approbation of their colleagues, such examples as "a specimen of staining with yellow, red, green, blue and purple colours; which would endure washing with warm water and soap"<sup>23</sup>. We can hardly believe that such primitive attempts at fast-dyeing could have interested the leading scientists of the day, if fast-printing of polychrome wall-hangings was simultaneously in "great practice" in London.

The second quotation comes from a letter in the records of the Royal African Society<sup>24</sup>, referring to "cuttanees, a sort stamped in England with flowers" (1678). Here again, however, the terms used are doubtfully associated with calico printing, for "cuttanees" were generally woven in a mixture of silk and cotton, and "stamping" might just as well refer to colourless embossing.

If we are right in taking Sherwin's 1676 patent as the beginning, we must next ask what it was that could have enabled him to be first in the field. The standard answer would be that he was fortunate enough to have discovered "the secret of the Indian chintzes with their brilliant fast colours", and this is in fact what Sherwin himself implied in the wording of his patent, which refers to "the only true way of East India printing and stayneing... never till now performed in our kingdom". The assumption is that he must have been the beneficiary of some smuggled information such as that which a Turk from Smyrna was supposed to have imparted to the two Dutch merchants who set up at Amersfoort two years later.

And yet a moment's reflection shows that it is by no means easy to understand exactly what this secret could have been. It certainly could not have been any actual method of printing, for it is well known that the high-class Indian chintzes which were imported into Europe were *painted* not printed, while all the evidence, including the wording of Sherwin's own patent, shows that the European imitations were *block-printed* from the start. Nor could the secret have lain in the particular dyestuffs used by the Indians, for they based themselves on indigo, and the chay root (akin to madder), the European equivalents of which had already been used by European dyers for centuries. Moreover the use of alum or iron mordants, which formed the basis of all Indian

madder-painting, was equally well known to European dyers.

Indeed, what we have to explain is not so much how it came about that Sherwin, and his Dutch counterparts at Amersfoort, discovered the Indian secrets in 1676 and 1678, but rather how it was that European dyers had not long ago taken the apparently small step from piece-dyeing mordanted cloth in madder to printing a design in mordant and subsequently dyeing in madder, and thus developed fast-dyed multi-coloured cloths similar to those which India seems to have been producing since the time of Pliny.

If we try and analyse what technical barriers could have for so long inhibited this decisive step from piece-dyeing to printing of the mordant and subsequent dyeing in madder, we find that the most serious difficulty must have been the problem of suitable thickeners. The alum or iron mordants, which could be used in a liquid form by the piece-dyers, had to be worked up into a viscous form before they could be satisfactorily block-printed. Suitable thickeners had to be found to produce this required viscosity, and thus to prevent the mordant from spreading beyond the printed areas. Moreover this presented a new problem in its turn, for the thickener had somehow to be removed from the cloth after the printing if its presence was not to reduce the effectiveness of the mordant in absorbing the madder during the subsequent dyeing.

These two apparently routine operations are so much a matter of detailed workshop practice that they have received very little attention from later writers, while relevant contemporary references are almost entirely lacking. Nevertheless, it can hardly be doubted that it is in them that we find the key to the birth of European calico printing. We can certainly claim the support of Persoz<sup>25</sup>, the most authoritative of all the earlier writers, in regarding the problem of thickeners as far more important than might be thought at first sight; and the same point has recently been elaborated in greater detail by Monsieur P. R. Schwartz of Mulhouse, the leading living expert<sup>26</sup>.

In the absence of any information from the seventeenth or early eighteenth centuries we can merely say that the European pioneers could have learnt nothing about thickeners from Indian practice, for the simple reason that according to all the evidence, the Indians painted on their mordants unthickened. We can only assume that it was a laborious process of trial and error which led to the empirical conclusion that starch and flour and various gums such as gum arabic and gum Senegal could all be used to produce that viscosity which was required before mordants could be satisfactorily printed by block. Not until the mid-eighteenth century do we have any positive information to go on, but we do then have two valuable contemporary references to the importance of thickeners to the English printers. The first is the Report of a Committee of the House of Commons in 1752<sup>27</sup>. The calico printers had presented a petition asking for a relaxation of the Royal African Company's monopoly in the

importation of gum Senegal, on the grounds that the company had imported none for several years, with the result that the price had increased eight times over the past nine years. Several of the leading printers, supported by linen-draper and merchants, gave evidence in which they emphasised that gum Senegal was essential as a thickener of certain mordants, both for block-printing and for "pencilling" (i.e. painting), and they described the disastrous consequences of trying to use substitutes. One printer went so far as to claim that he had tried "every thing that was glutinous in the vegetable kingdom, but without success". Despite the opposition of one or two brokers who seem to have been making money from the shortage, the House acceded to the printers' pleas and gave permission for imports from Europe. Although this evidence is too late to be directly relevant to conditions in the 1670's, it at least proves that it is not fanciful to suppose that the use of the correct thickeners may have been one of the basic difficulties which delayed the initial development of European printing for so long. The second piece of evidence from the mid-eighteenth century is to be found in the well known notes of Jean Ryhiner, the Basle printer, dating from 1766<sup>28</sup>. He specifically says that in his view the superiority of the English printers (he is particularly thinking of copper-plate work) is based almost entirely on their use of the correct thickeners.

It is perhaps appropriate to mention here a later British contribution to the chemistry of thickeners—namely the development of torrefied starch, which soon came to be known universally as "British gum". As usual English references to its discovery are almost entirely lacking, and it has so far proved impossible to pin down the exact time or place of its first use. A story about its accidental discovery following a fire in a Dublin starch factory seems altogether too picturesque<sup>29</sup>, although it seems clear that Duffey's printworks at Ballsbridge, outside Dublin, was among the first to use it, and the name "British" rather than "English" speaks in favour of an origin in Ireland rather than in Lancashire. The earliest reference so far traced dates from 1813<sup>30</sup>, and it seems likely that its first use cannot have been much earlier, for Samuel Parkes, a practising printing-chemist, describes how in 1817 he was called in to help prove to the Excise officers that a stock of "British gum" on which they had claimed the starch duty at a Rotherham drysalers, was in fact a new and entirely different product, and therefore not liable for duty<sup>31</sup>.

One other apparently unimportant and routine operation must also be mentioned as undoubtedly contributing to the European backwardness in mordant printing, namely the problem of "clearing" the white parts of the pattern. When a mordant-printed cloth is first removed from the madder bath the dye will be found to have partially coloured the whole cloth so that even the unprinted parts of the pattern have taken on a reddish hue. Quite an elaborate series of operations, including

bleaching in the sun, aided by immersion in cowdung or a solution of bran, were found in practice to be necessary before the unprinted areas became white again, and a good deal of empirical experimenting was certainly needed before the best method of achieving this could be discovered.

The European delays in solving these seemingly simple problems of "thickening" and "clearing", can only be understood if account is taken of the decisively different reactions of madder to animal and vegetable fibres respectively, and in particular of the impossibility of "clearing" unmordanted areas in the case of wool by contrast with cotton. This contrast certainly helps to explain why India, with cotton as its staple fibre, passed from mordant dyeing to mordant painting so early, while Europe, with wool as its staple, supplemented with silk, was so long in taking this decisive step. Although this leaves unexplained why German or Scottish linen was not used instead—for it would have been little inferior to Indian calico as a medium for madder-printing—there can be little doubt that it is here that one of the decisive factors in the European backwardness is to be found.

It would not be right to leave this question of the origins of European calico printing without mentioning that the late Monsieur Henri Clouzot, by far the most prolific and most quoted French authority, drew a very different picture of these early developments in his numerous articles and books<sup>32</sup>. He believed that printing started much earlier in France than in the rest of Europe—perhaps as early as the 1650's—but was nipped in the bud by the repressive legislation of 1686 (passed in the interests of the Lyons silk-weavers), before it had time to reach the stage of producing anything more than crude and fugitive imitations of the Indian chintzes. Printing remained prohibited until 1759, but immediately after the removal of the ban, French printers, led by Oberkampf at Jouy, were quickly able for the first time to produce fast-dyed chintzes on the basis of careful reports of the secret Indian methods which had been painstakingly obtained and published by French envoys in the 1740's. Clouzot tended to generalise these abnormal French conditions into a theory which implied that European calico printing as a whole first went through a seventeenth century stage of fugitive ("petit teint") printing, and was only able to advance to proper calico printing ("bon teint") in the mid-eighteenth century as a result of the intervening French discovery of the "secrets of the East". It will be seen that this picture differs radically from that which we have drawn from English evidence.

Clouzot was undoubtedly right in thinking that textile printing developed considerably earlier in France than in either England or Holland. He himself, however, never traced any detailed documentary evidence to throw light on its nature, and it remained for a later writer<sup>33</sup> to discover clear proof that at least in Marseilles (which was favoured by special customs dispensations) block-printing of some sort was already established as early as 1648, and moreover that block-printing with fast-dyed madder colours was probably



already being practised not much later. Had this information been available to Clouzot he would certainly have had to modify his belief that the pre-prohibition French printers worked only with fugitive colours.

But even without this new French evidence, we should surely be justified in assuming that the products of William Sherwin and his larger English associates must have been fast-dyed<sup>34</sup>. How otherwise can we explain their popularity? As we have seen, the wool and silk interests tried to ban them in 1696<sup>35</sup>. They failed, but succeeded in 1700 in prohibiting the import of Indian chintzes<sup>36</sup>. As this merely transferred the demand to the home-produced imitations, they renewed their attacks on these and finally had them banned also (except for export) in 1721<sup>37</sup>. In the course of this prolonged campaign an enormous number of anti-chintz pamphlets were produced<sup>38</sup>, incorporating every possible argument that could be used against the new industry. Among them one finds many picturesque details about the popular mania for chintz, but never does one find the argument that the home-made products were shoddy substitutes for the Indian originals, with worthless colours fugitive to sun and soap. In face of this, one can hardly doubt that the infant English industry was based from the start on real and not false calico printing.

Concerning the search for the true Indian "secrets" in the 1730's and 1740's, there is no doubt that the French took the most energetic and systematic steps to discover the exact methods used by the Indian chintz-painters at that time, the details of which have recently been dramatically added to and brilliantly summarised by Monsieur Schwartz in the *Journal of Indian Textile History*<sup>39</sup>. However, M. Schwartz makes it clear that he does not share Clouzot's belief that this proves that no European printers before this date were capable of printing in fast colours, and he takes it for granted that the pre-prohibition French printers, and their English and Dutch counterparts, were able to do so. He suggests that this ability depended on the transmission to Europe of various workshop procedures from the Near East (and in particular from Turkey) rather than from India itself. The recondite references which he assembles in support of this thesis are admittedly fragmentary and ambiguous, but they seem to be supported by the tradition that the first Dutch printers at Amersfoort were helped by a Turk from Smyrna, and by the definite evidence of Levantine Armenian printers in Marseilles. Whether William Sherwin likewise gained his special knowledge from some contact with the Near East, or perhaps acquired it at second-hand from the French, we shall presumably never know.

All these problems would, of course, be much more easily elucidated if more textiles from this period had survived. There is certainly no doubt that Clouzot's pessimistic theory about European technical backwardness in the first half of the eighteenth century must have been strongly influenced by the very low quality of the earliest examples of which he was aware—namely some

miserable specimens incorporated into the *Journal Economique* for June 1755, first published and illustrated in colour by Edgard Depierre in 1912<sup>40</sup>. Until very recently there has been almost nothing tangible to set against this except the technical competence of the earliest known English example<sup>41</sup>, but as this solitary specimen dated from only four years earlier—that is 1751—it was still much too late to provide testimony to printers' skills at the beginning of the century. However, during the visit to the United States last year it was found that one of the business letters, dated December 1726, in the so-called Alexander papers in the Library of the New York Historical Society had pinned to it twenty-nine tiny samples of English printed textiles<sup>42</sup>. These are by far the earliest precisely datable surviving English printed textiles, and carry the story back a full quarter-century. A careful examination of these samples (Fig. 1) showed that the majority, and probably all, were printed in fast-dyed madder colours. We can therefore regard them as going some way towards confirming our claim that English calico printing was based on fast colours from its earliest days. It can hardly be doubted that even earlier examples, lying similarly buried in business archives, will ultimately come to light.

In this article we have dealt with the origins of English calico printing almost exclusively in terms of madder-style printing, as forming the main basis of all European printing right up to 1800 and beyond. In the next article we shall tackle the parallel development of indigo dyeing and printing, a field in which the early English printers made some of their most important—and most neglected—contributions.

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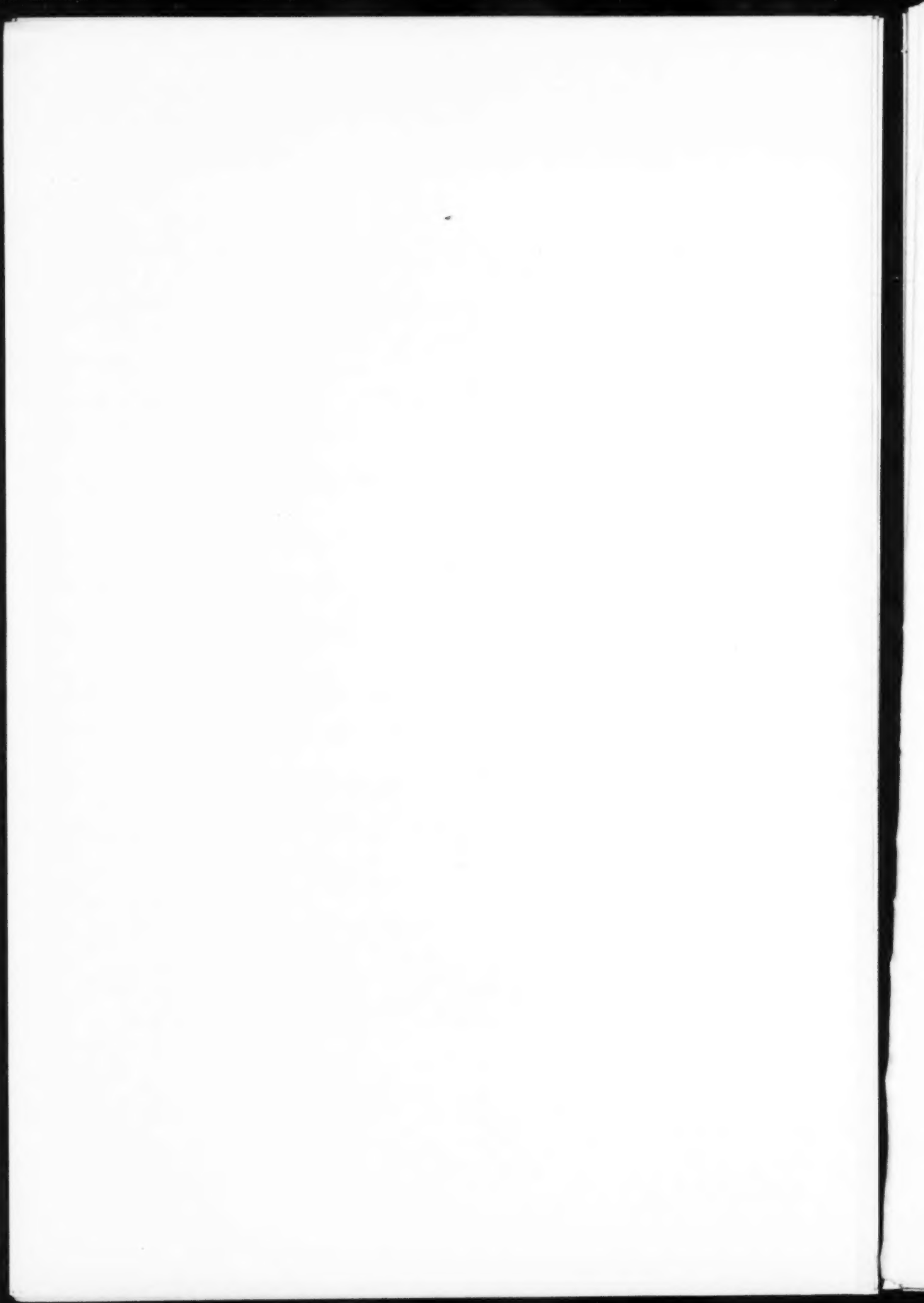
(Received 25th May 1959)

#### Notes

- <sup>1</sup> The exhibition was accompanied by a catalogue, *English Chintz, Two Centuries of Changing Taste*, and a picture-book, *English Chintz*, both published by H.M. Stationery Office on behalf of the Victoria and Albert Museum.
- <sup>2</sup> Made possible by the generosity of the Henry Francis Du Pont Museum at Winterthur, Delaware.
- <sup>3</sup> Made possible by a generous grant from the Trustees of the Leverhulme Research Awards.
- <sup>4</sup> *Op. cit.*, p. 259.
- <sup>5</sup> *Parliamentary Papers*, vi (1833), answer to question 3821.
- <sup>6</sup> Parakunnel J. Thomas, *English Historical Review*, 39, (154), 206-216 (April 1924).
- <sup>7</sup> Of all the seventeenth century patents sometimes claimed as referring to calico printing, only two could really be relevant, namely, George Wood's (No. 14, 1619)—about which we know nothing—and William Sherwin's (No. 190, 1676)—discussed below. Those of Togood (1675), Bagley (1692), and Poussett (1694) are concerned with wool or silk.
- <sup>8</sup> R. Crisp, *Richmond and its Inhabitants* (London 1866), p. 115.
- <sup>9</sup> Geoffrey Turnbull, *A History of the Calico Printing Industry of Great Britain* (Altrincham 1951), p. 18.
- <sup>10</sup> John Stirling, "History of Colour Printing in the United Kingdom". A paper read to the Manchester Section on 19th December 1902, and published in the *Journal* (19, 36-40 (Feb. 1903)). Some of Stirling's statements seem to have been based on early documents which have disappeared. Any information about their present whereabouts would be very welcome.



Fig. 1—English Printed Patterns dated December 1726



- <sup>11</sup> Alice Dreyer, *Les Toiles Peintes en Pays Neuchâtelais* (Neuchâtel 1923).
- <sup>12</sup> Dorette Berthoud, *Les Indiennes Neuchâtelaises* (Boudry 1951).
- <sup>13</sup> *European Printed Textiles* (London: H.M.S.O., 1949), p. 6.
- <sup>14</sup> *Histoire de la Manufacture de Jouy et de la Toile Imprimée en France* (Paris 1928), Vol. I, p. 4.
- <sup>15</sup> House of Lords MSS. (4th April 1696).
- <sup>16</sup> *Historical Manuscripts Commission Reports*, House of Lords MSS., New Series, Vol. II (1903), Section 1050, p. 242.
- <sup>17</sup> Unless it is assumed that Peter Mauvillain, who was printing at Tooting in 1714, was already there when he signed the 1696 petition.
- <sup>18</sup> Peter Casteels, the flower-painter, is said to have worked for a calico printer at Tooting in 1735, and to have moved with him to Richmond at some time between then and his death in 1749. Vol. IV (1771), p. 11.
- <sup>19</sup> Public Record Office, Colonial Office MSS., Section 388, Part II, p. 223.
- <sup>20</sup> First illustrated in F. W. Phillips, *Old English Chintzes* (Hitchin 1912). Reproduced in the *Journal* (71, 377, Fig. 5 (1955)).
- <sup>21</sup> L. A. Driessen, "Calico-Printing and Cotton Industry in Holland", in *Ciba Review*, Special Number on Dutch Textile Printing, No. 48 (May 1944).
- <sup>22</sup> Vol. II, p. 159.
- <sup>23</sup> G. P. Baker, *Calico Printing and Printing in the East Indies* (London 1921), p. 31.
- <sup>24</sup> Thomas Birch, *History of the Royal Society of London*, 1756-7, Vol. II. Entries for Nov. 11th and Dec. 9th 1669, pp. 401 and 411. For some reason this date has been consistently misquoted as 1696 for over a century, e.g. by W. H. von Kurrer, *Geschichte der Zeugdruckerei* (Nuremberg 1840), p. 148; and MacIver Percival, *The Chintz Book* (London 1923), p. 77.
- <sup>25</sup> Royal African Company, Letter Book T 70/20, 17/9/1678.
- <sup>26</sup> J. Persoz, *Traité théorique et pratique de l'Impression des Tissus* (Paris 1846), Vol. II, p. 163 et seq.
- <sup>27</sup> P. R. Schwartz, in *Journal of Indian Textile History* (Ahmedabad 1957), Vol. III, p. 42.
- <sup>28</sup> *Journals of the House of Commons* (Jan. 17th and Feb. 18th, 1752).
- <sup>29</sup> First published in Dollfus-Ausset, *Matériaux pour la Coloration des Etoffes* (Paris 1865), Vol. II, p. 16.
- <sup>30</sup> Mrs. Ada Leask, whose researches have thrown so much light on the early history of calico printing in both Ireland and England, reports that one vivid account which she has tracked down is riddled with inconsistencies.
- <sup>31</sup> Edward Bancroft, *Experimental Researches concerning the Philosophy of Permanent Colours* (2nd edition, London 1813), Vol. I, footnote to p. 362.
- <sup>32</sup> Samuel Parkes, *Chemical Essays* (2nd edition 1823), Vol. I, p. 629, note 47.
- <sup>33</sup> Cf. in particular *La Manufacture de Jouy et la Toile Imprimée au XVIII<sup>e</sup> Siècle* (1926), pp. 6-8.
- <sup>34</sup> H. Chobaut, "L'Industrie des Indiennes à Marseilles avant 1680", in *Mémoires de l'Institut Historique de Provence*, Tome XVI (Marseilles 1939), pp. 81-91.
- <sup>35</sup> Sherwin himself, in his evidence before the Lords (see note 15 above), states that their woollens will not bear washing. As the whole inquiry was directed to the question of cotton printing, I take this to imply that their claims to fast-printing were limited to cottons. In Thomas's article (see note 6 above) Sherwin's statement is misquoted as referring to cotton as well.
- <sup>36</sup> MacIver Percival (*op. cit.*, p. 34) claims that the wool and silk interests did not bother to attack the English prints as well as the Indian imports until well into the eighteenth century, and therefore concludes that they could not have been fast-dyed in the earlier days. He seems to have been unaware of the efforts which were made in 1696 to get the anti-Indian bill amended to prohibit the home-prints as well.
- <sup>37</sup> 11 & 12, Will. III, c.10.
- <sup>38</sup> 7 Geo. I, St. 1, c.7.
- <sup>39</sup> For a list of some of the most important, see the bibliography in P. J. Thomas, *Mercantilism and the East India Trade* (1926).
- <sup>40</sup> P. R. Schwartz, "French Documents on Indian Cotton Printing", in *Journal of Indian Textile History* (Ahmedabad), 2 (1956) and 3 (1957). The definitive French version appeared in *Bull. Soc. industr. Mulhouse* (4) (1957) and (5) (1958).
- <sup>41</sup> *La Toile Peinte en France au XVII<sup>e</sup> et au XVIII<sup>e</sup> Siècles* (Paris, 1912).
- <sup>42</sup> A coverlet, block-printed by George Ormerod of Wallington. For illustration, see *J.S.D.C.*, 71, 377 (1955), Fig. 7.
- <sup>43</sup> The samples were apparently sent back by James Alexander, a New York importer, for matching when ordering new supplies from David Barclay & Son, a leading general shipper in London. I am indebted to Mr. Calvin Hathaway, the Director of the Cooper Union Museum, York, for having first drawn my attention to the importance of the Alexander papers.

## EXTERNAL ADDRESS

## Effect of Structure on the Change in Colour of Vat Dyes on Soaping\*

J. WEGMANN

After a general survey of the problem of the changes in colour which accompany the soaping of vat dyes, it is shown that, at least for a limited range of dyes, the 1,4-dibenzamidoanthraquinones, such changes must be due to changes of a molecular character. A working hypothesis has been evolved according to which the different forms are to be regarded as representing a new type of isomerism, termed *contact isomerism*, and can be visualised as partly existing in solid form, and in isolated cases even as crystalline modifications, in conformity with the earlier hypothesis of different polar forms. The marked effects of certain substituents on the colour, hitherto inexplicable, can be explained by a predominating effect on the resulting isomeric composition, acting alongside the normal effect of the substituents. Various anomalies that can occur during development can be readily explained on this basis.

## 1. INTRODUCTION

A "soaping" with boiling soap or detergent solution is essential with vat dyeings in order to stabilise the colour and obtain the best fastness properties. The accompanying changes in colour, which are sometimes very characteristic, have aroused great practical and theoretical interest.

At first it was thought that incomplete reoxidation might be the cause, but later this was replaced by dye aggregation<sup>1</sup>. This idea was developed into the theory that the dye particles undergo a transition from the amorphous through the molecular to the crystalline state<sup>2</sup>. This theory was generally accepted, although it was pointed out that some facts could not possibly be explained on this basis<sup>3</sup>.

Observations in support of the molecular character of the differences between soaped and unsoaped dyeings were published in 1953<sup>4</sup>, but at about the same time Sumner, Vickerstaff, and Waters<sup>5</sup> described investigations which, in their opinion, confirmed the crystallisation theory. In spite of a number of discussions<sup>6</sup>, the experimental evidence then available was insufficient to decide between the two theories.

Since then extensive experimental material has been collected, and it has been found that the molecular theory gives a better understanding of certain relationships between colour and constitution, which could not previously be explained. Furthermore, interesting connections have been found between the behaviour of vat dyeings and certain phenomena of interest in the chemistry of organic pigments.

On account of the scope and the complexity of the problems involved, the present discussions are restricted to the 1,4-diaroylaminoanthraquinone dyes.

## 2. FUNDAMENTAL NATURE OF THE MOLECULAR THEORY

It is essential to appreciate that, in contrast to the crystallisation theory, the molecular theory, fundamentally, is purely an assertion. According to the former, the colour change is due to a transition of the dye from the molecular to the crystalline state. The cause of the phenomenon is thus a change in physical state, and this affords an explanation of the process, whilst the molecular theory merely states that the colour change is due

to changes in the individual dye molecules: what kind of changes these are, and why they occur, remain open questions. Thus with the molecular theory the work has only started; whereas with the crystallisation theory it is ended, and the problem can be regarded as solved.

The mechanism of cellulose dyeing offers a parallel case. The colloidal theory<sup>7</sup> asserted that the affinity of direct dyes is a consequence of the optimum aggregation of the dye molecules in solution. Boulton and Morton<sup>8</sup>, on the other hand, showed that in fact only single dye molecules can diffuse into the fibre, and are adsorbed there in an oriented manner. The molecular theory thus established how dyeing occurs, and showed that aggregation in solution is not the cause of substantivity, which was again a completely open question. But there was now a sound basis on which to attack this problem.

The molecular theory forms also the most important basis for investigating and explaining the colour changes of vat dyeings.

## 3. PREVIOUS WORK

Investigations published before 1953 have already been discussed in detail<sup>4,5</sup>, and the following brief comments refer only to papers which have appeared since then.

The most important publication is that by Sumner *et al.*<sup>5</sup>, who consider the crystallisation theory to be confirmed, especially by the analogous colour changes occurring in colloidal solutions of vat dyes, and the accompanying increase in particle size and crystal growth, which they observed with the aid of the electron microscope. They cite also the increase in the degree of orientation occurring on soaping, as shown by the dichroism of the dyeings. The great differences in effect between different dyes are ascribed to variations in crystal growth.

Joss<sup>9</sup> regards his results on the soaping of vat and azoic dyeings as confirming the molecular theory.

Schäffer<sup>10</sup> revives the idea, first suggested by Scholl<sup>11</sup>, that the colour change is due to incomplete reoxidation of the dye in the fibre, supporting this view with evidence that in certain cases, when a colloidal solution of an oxidised vat dye is mixed with a vatted solution of the same dye, a colour corresponding to that of an unsoaped

\* Paper presented at the I.F.A.T.C.C. Congress held at Church House, Westminster, 16th–18th September 1959



dyeing results. However, such visual correspondence is purely accidental, and is not connected with the colour of unsoaped dyeings, as can be shown by comparing the absorption spectra of such colloidal solutions with those of the dyeings.

Egerton and Galil<sup>12</sup> point out the parallelism between the colour of soaped dyeings and that of the dye in the solid state. They ascribe the colour change to association by means of hydrogen bonds, and with indigoid dyes they assume also a transition from the *cis* to the *trans* isomer, thus to some extent accepting the molecular theory. However, their demonstration that dyes in the crystalline form have the highest light fastness led them to the view that, in the case of soaped dyeings, crystals of dye are embedded in the fibre.

#### 4. STARTING POINT

The following observations have been adduced in support of the molecular theory—

(1) In various cases there is no parallelism between the dichroism of a soaped dyeing and that of the dye in crystal form.

(2) In some cases addition of methanolic caustic potash produced in organic-solvent dye solutions similar colour changes to those accompanying the soaping of dyeings.

(3) Analogous colour changes are sometimes produced by adsorption of dye from organic-solvent solution on activated aluminium oxide.

Since aluminium oxide is known to be able to polarise polarisable molecules<sup>13</sup>, the postulated molecular changes were interpreted in terms of molecular forms of different polarity, one of which is favoured by soaping. This interpretation has been chosen because it is to be regarded as the most general formulation. No inquiry has been made as to the underlying causes—e.g. as to how far isomeric forms like *cis-trans*, amide-iminol, etc., are involved, solely or in part—as insufficient experimental evidence is available to decide such questions: they must be considered separately for each constitutional type of vat dye.

The above hypothesis is supported by the fact that the final colour developed by dyeings on being soaped at the boil can be obtained also by treating them with polar solvents in the presence of water. Even dyeings normally requiring 30 min. soaping at the boil, such as Cibanone Red F6B (C.I. 70320), can be "developed" practically instantaneously at room temperature. In some cases this method proved itself more effective than soaping at the boil, and it was possible to obtain colours which are hardly if at all attainable by soaping. In other cases, however, this method produced different, undesirable colours, so that a broad practical evaluation has not yet proved possible.

That the transition from the molecular to the crystalline state cannot be regarded as the cause of the observed colour changes was deduced also from certain parallels between the behaviour of various polymorphic crystal forms<sup>14</sup> of a dye, e.g. indanthrone, and that of soaped and unsoaped dyeings.

#### 5. NATURE OF AFTERTREATMENT

The main requirement for bringing about the colour change of a vat dyeing, and hence stabilising its colour, is damp heat. "Development" can thus be achieved by steaming as well as by boiling. With dyeings which are easily developed, even immersion in cold water for a fairly long time is sometimes sufficient. For dyeings which are difficult to develop, however, high temperature is very important in obtaining complete development within a reasonable time. Additions, e.g. soap and synthetic detergents, play only a comparatively minor part.

Polar substances as a rule yield the same colour as soaping at the boil, but with certain dyes other colours may result. Among the compounds which may be regarded as especially effective the following may be mentioned: pyridine, cyclohexylamine, aniline, nitrobenzene, benzonitrile, toluene-sulphonamide, benzyl alcohol, acetone, ethyl acetate, ethylene chloride, dimethylformamide, etc., which are used either as solutions or in the form of emulsions. There is no direct relation with the dipole moment, and the presence of water is necessary.

#### 6. CHARACTER OF COLOUR CHANGES

Depending on the individual dye, the changes can be very great, and may be in either a bathochromic or a hypsochromic direction. In other cases the change may be hardly noticeable, and in a few cases there is practically no change at all. A typical case is 1,5-dibenzamidoanthraquinone (Cibanone Yellow FGK, C.I. 61725), which undergoes a considerable change, which is very noticeable in the absorption maximum (445 → 462 mμ.) as well, whilst the corresponding *p*-chloro derivative shows hardly any change (445 mμ.).

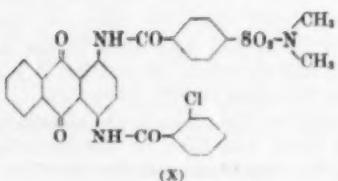
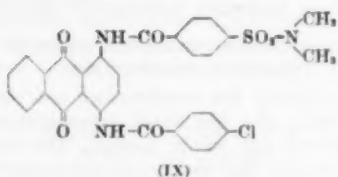
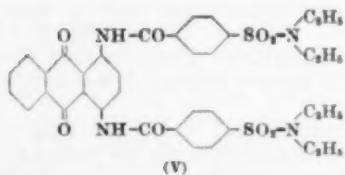
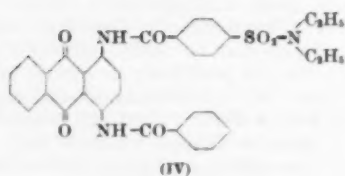
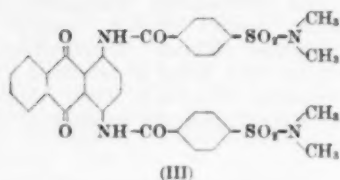
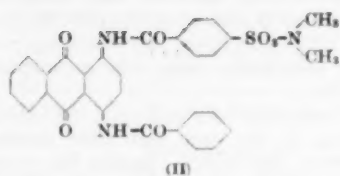
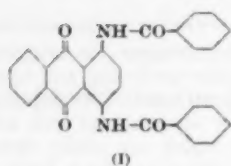
A strong bathochromic shift is found with Indanthren Brilliant Violet BBK (C.I. 63355), whilst dibenzanthrone (Cibanone Dark Blue FBO, C.I. 59800) shows a change in the hypsochromic direction.

These phenomena, which vat dyes have in common with azoic dyes, are not limited to certain constitutional subgroups, but can be observed in all classes, such as the indigoid and anthraquinonoid dyes and derivatives of more highly condensed ring systems, including heterocyclic systems.

#### 7. DEPENDENCE OF COLOUR CHANGES ON CHEMICAL CONSTITUTION

It is essentially the constitution, not the mode of application, of a dye which determines whether or not there is any colour change. The necessary condition is only that the dye should be applied *via* a temporarily water-soluble form, and not directly in the form of a pigment. Thus a similar change of colour is observed whether the dye is applied as the water-soluble sulphuric ester of the leuco compound (Indigosol) and fixed in the fibre by hydrolysis and oxidation, or whether it is applied directly in the alkali-soluble leuco form.

Very small modifications in the constitution, on the other hand, can have an unexpectedly great effect on the magnitude and the direction of the



- (a) Unsoaped  
(b) Soaped

FIG. 1—Dyeings on Cotton of Dyes II, III, IV, and V

- (Above)  $\alpha$ -form  
(Below)  $\beta$ -form

FIG. 6—Polymorphic Crystal-modifications of Dye II

- (a) Unsoaped  
(b) Soaped  
Dope-dyed Viscose Rayon  
(a) With the  $\alpha$ -modification  
(b) With the  $\beta$ -modification

FIG. 9—Dyeings on Viscose Rayon of Dye III

- (1) 2% Dye II  
(2) Mixture of 1% Dye II and 1% Dye I  
(3) 2% Dye I

FIG. 17—Unsoaped (a) and Soaped (b) Dyeings on Viscose Rayon

- (1) 2% Dye IX; 2% Dye X  
(7) 2% Dye I  
(2-6) 2% Mixtures of IX + I and X + I  
in different molecular ratios

FIG. 19—Unsoaped (a) and Soaped (b) Dyeings on Viscose Rayon

FIG. 10—Soaped Dyeing on Ramie of Dye II in Polarised Light (vector parallel to the red fibre)

FIG. 25—Stuart-Brigleb Molecular Model of the Leuco Form of Dye III adsorbed on a Cellulose Chain

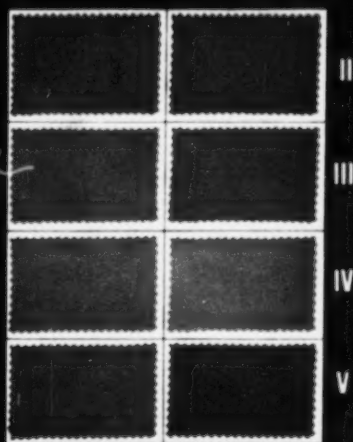


Fig. 1

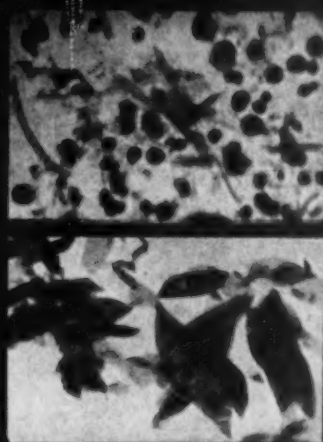


Fig. 6

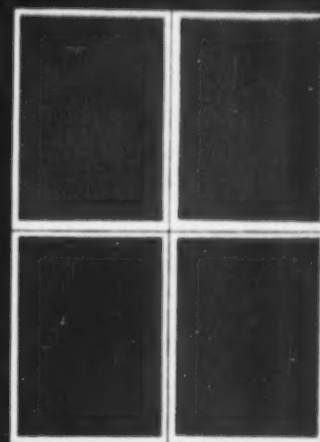


Fig. 9

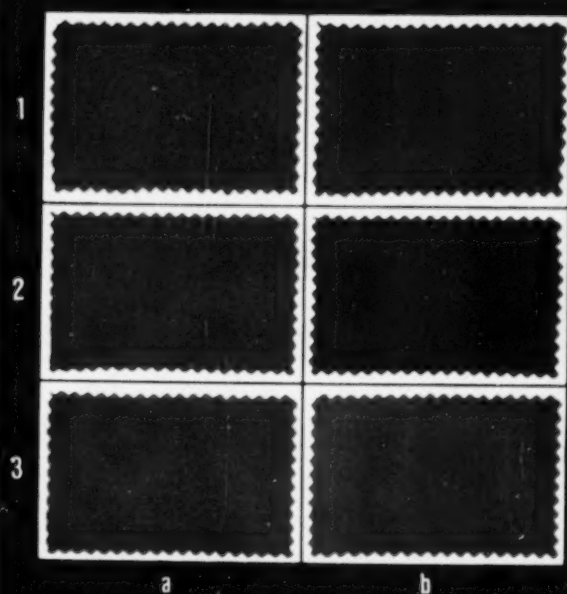


Fig. 17

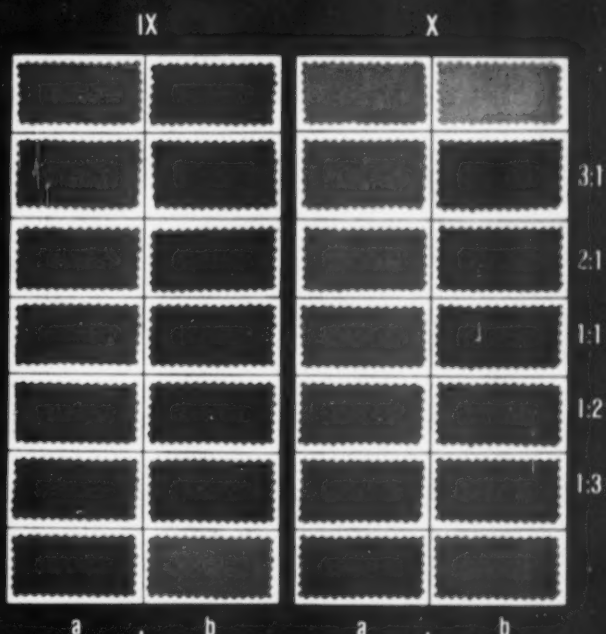


Fig. 19

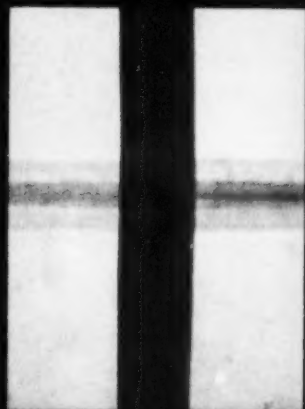


Fig. 10

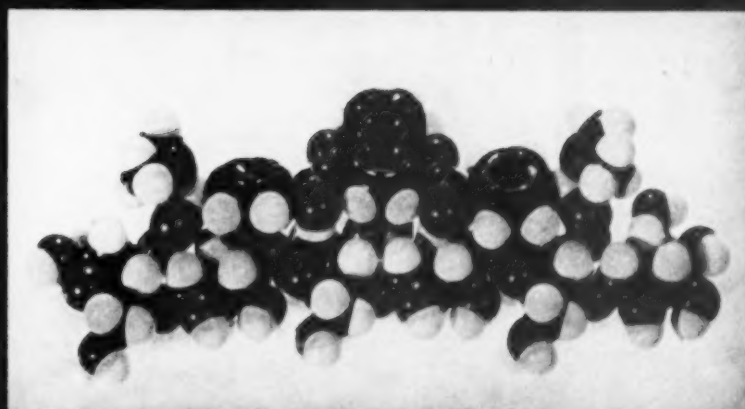


Fig. 25

Fig. 32-35  
Unsoaped (a) and  
Soaped (b) Dyes  
on Cellophane

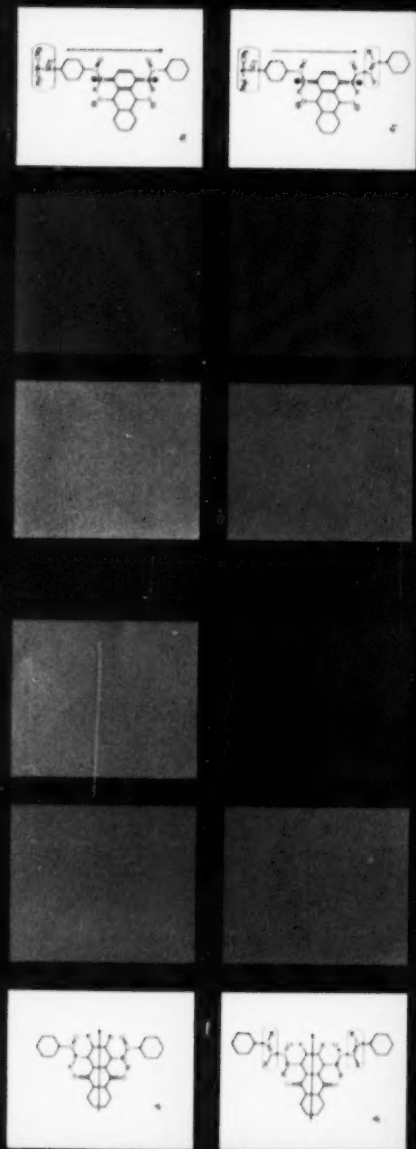


Fig. 34



Fig. 35



colour change, as has been shown above for Cibanone Yellow FGK.

With pyranthrone (Cibanone Golden Orange FGN, C.I. 59700), which changes from reddish orange to yellowish orange, the introduction of halogen atoms produces a stepwise decrease in the difference between soaped and unsoaped dyeings. The shade is, in effect, stabilised in the reddish-orange form.

Dibenzanthrone (Cibanone Dark Blue FBO) behaves in a similar manner. With the trichloro derivative the change even occurs in the opposite bathochromic direction. An unaccountably great effect on the colour of the soaped dyeing, i.e. on the change on soaping, is produced by different alkyl groups in the dipyrzoleanthronyl series. Koch<sup>3</sup> has investigated and described this in detail. He was the first to point out that it was not possible to explain these differences on the basis of differences in the tendency to aggregate, and that other, more specific causes must be assumed.

Our present knowledge of the effect of substituents on colour is not sufficient for the understanding of the effects observed by Koch.

Halogen atoms do not always decrease the change in colour, as can best be seen with the 1,4-dibenzamidoanthraquinone series, where, in contrast to the 1,5-series, the introduction of halogen atoms leads to a big colour change on soaping.

Other groups as well, e.g. methoxy, alkylsulphonyl, and sulphonamoyl groups, in some cases produce in this series very great colour changes between unsoaped and soaped dyeings. As different substituents are interdependent in their effect, the individual effects may either strengthen or cancel one another. The whole matter is in consequence very complex. Especially striking is the peculiar effect of different sulphonamoyl groups, as can be seen from the following series. One dimethylsulphonamoyl group causes the development from brownish orange to brilliant red, a second such group suppresses the effect, whilst with diethylsulphonamoyl the effect is reversed (Fig. 1).

#### 8. EFFECT OF SUBSTRATE

The nature of the textile substrate can influence both unsoaped and soaped colours, and in consequence may determine the extent of this change and sometimes even its nature. Thus with dibenzanthrone a marked hypsochromic shift from bluish violet to reddish violet is observed on viscose rayon, a smaller change on cotton, and practically no change on nylon, the reason being that the soaped colour is not very different from the unsoaped one. But the unsoaped colour as well may be responsible for the resulting difference. For instance, practically no change of colour takes place when dimethoxydibenzanthrone (Cibanone Brilliant Green FBF, C.I. 59825) is applied to cellulosic fibres, but a change is observed on polyvinyl alcohol fibres because the unsoaped colour is much bluer in this case. The difference in light fastness between the unsoaped and soaped dyeings is correspondingly much greater here than on cellulosic fibres.

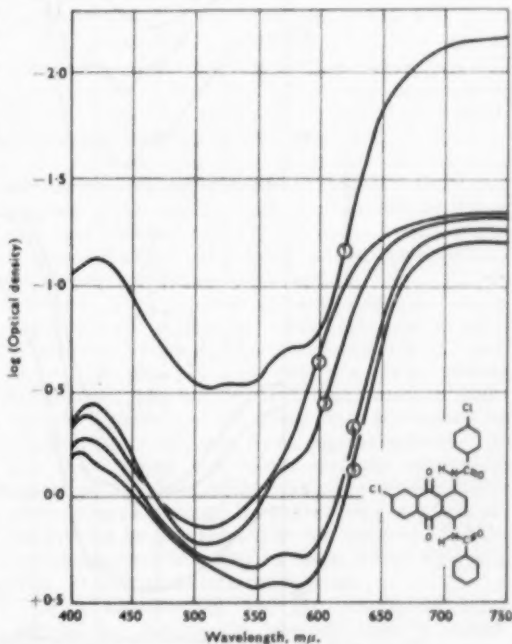
It is noteworthy that in certain cases the dye is developed to entirely different shades on cotton and on regenerated cellulose, e.g. with 1,4-bis-*p*-dimethylsulphonamoylbenzamidoanthraquinone (III) (cf. Fig. 1 and 9).

Still more astonishing and of special theoretical interest is the case of 1-*p*-dihydroxyethylsulphonamoylbenzamido-4-benzamidoanthraquinone, which on cotton changes from brownish red to yellowish red, and on viscose rayon from brownish red to violet. Although the dye itself has no tendency to yield streaky dyeings, streakiness can result on viscose rayon from "uneven soaping".

#### 9. EFFECT OF INTERMEDIATE DRYING

It was observed, quite unexpectedly, that the development of a dye on a given fibre can vary according to whether the dyeing is dried before soaping or is aftertreated immediately after reoxidation, and this led to many difficulties at the start of the investigations.

A typical example is 1-*p*-chlorobenzamido-4-benzamido-7-chloroanthraquinone (VI): if soaping follows immediately after reoxidation, the dyeing turns from brownish red to bluish violet; but after air-drying only a red-violet is obtained, irrespective of how long a time soaping is continued at the boil. The resulting colour is reproducible, and represents a definite intermediate form. With ethylene chloride, however, it is possible to develop a dried unsoaped dyeing to bluish violet (Fig. 2). All the forms can be converted into one another by revatting.



- (1) Alkaline colloidal solution of the reoxidised dye
- (2) Unsoaped dyeing on Cellophane
- (3) Dried and soaped dyeing
- (4) Soaped immediately after reoxidation
- (5) Dried and developed in ethylene chloride in aqueous alcohol

FIG. 2.—Absorption Curves for 1-*p*-Chlorobenzamido-4-benzamido-7-chloroanthraquinone (VI)



## 10. ANALOGOUS PHENOMENA IN THE ABSENCE OF A SUBSTRATE

From the foregoing it can be seen that the unsoaped colour represents a metastable form, which can be more or less stabilised by the substrate. The question arises, therefore, whether phenomena analogous to those observed on soaping can occur even in the absence of a textile substrate.

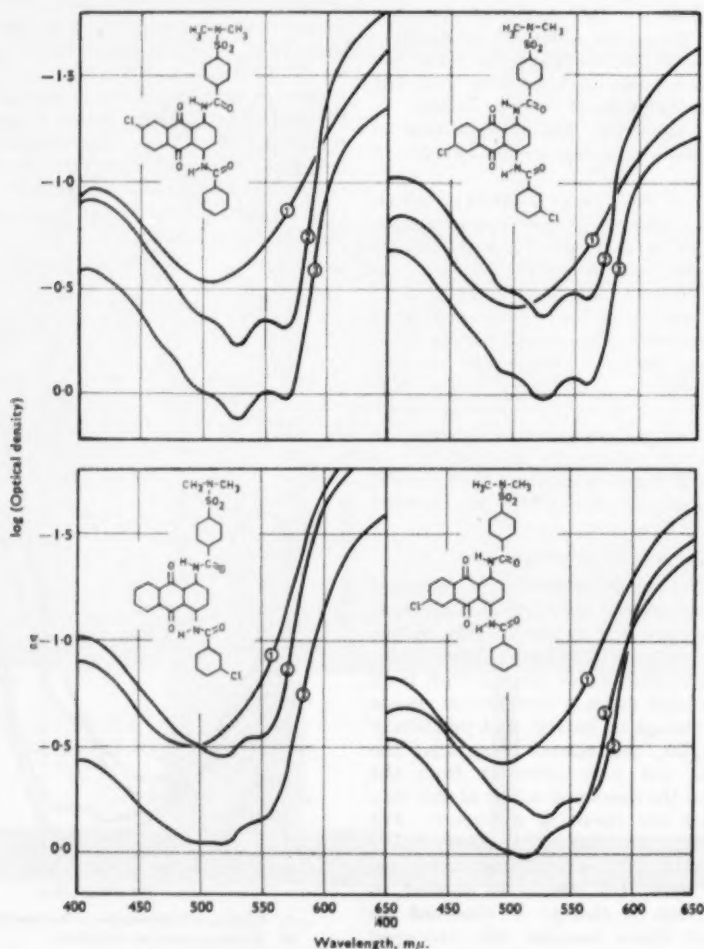
If a leuco vat dye is reoxidised, e.g. by blowing air through the aqueous solution, precipitation of a metastable form may occur, which by subsequent heating of the aqueous dispersion, or by recrystallisation from organic solvents, may be converted into a stable form<sup>14</sup>. Whether this can be done depends to a great extent on the experimental conditions, but also depends on the choice of dye, the modified form of which must have sufficient stability for it to be isolated in substance.

For comparisons with dyeings, the most suitable method is reoxidation of the leuco compound in the

form of a colloidal solution<sup>8</sup>. As a rule colloidal solutions of remarkable stability are obtained, the colour and absorption spectra of which normally agree with those of the soaped dyeing (Fig. 3).

If reoxidation is carried out slowly by shaking, or if the medium is slightly acid, it is possible with a number of dyes to obtain colloidal solutions corresponding to the metastable unsoaped form (Fig. 4). These solutions, however, are unstable, and on standing for some time, or on heating, precipitation occurs as a result of increase in particle size, and in a form corresponding to the soaped dyeing. The colloidal solutions obtained directly in the soaped form do not change, either on heating or on standing for a long time. From this it follows that there is no connection between particle size and colour.

With dyes which are difficult to "develop", e.g. III, a form similar to that of the unsoaped dye is obtained by blowing the vat into a cold alkaline peroxide solution, and only by using a peroxide



- (1) Unsoaped dyeing on Cellophane
- (2) Alkaline colloidal solution of the reoxidised dye
- (3) Soaped dyeing

FIG. 3

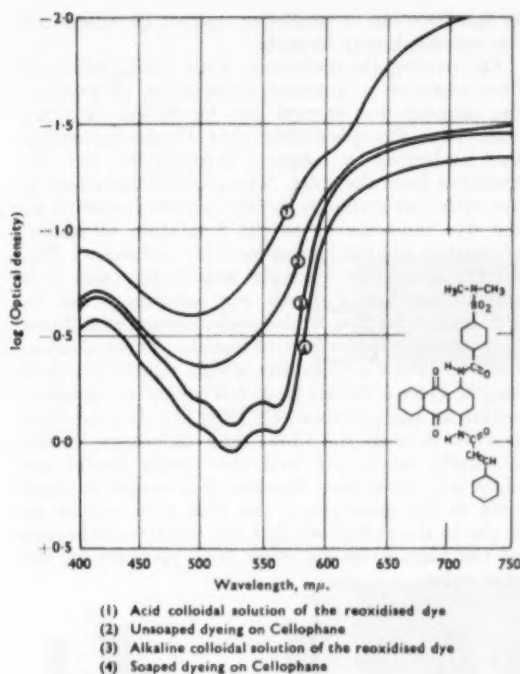


Fig. 4—Absorption Curves for 1-*p*-Dimethylsulphamoylbenzamido-4-cinnamidoanthraquinone (VII)

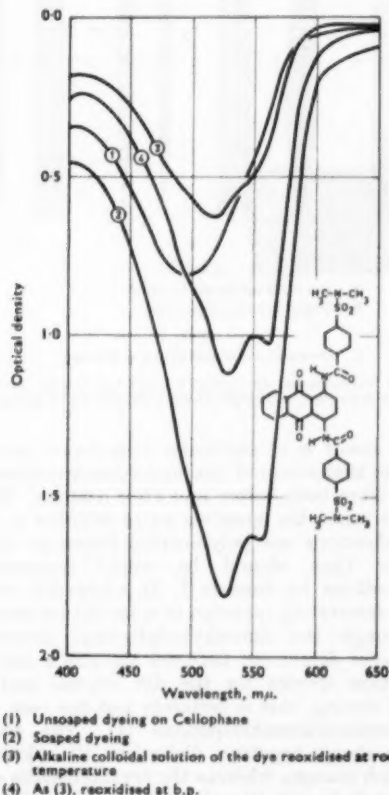


Fig. 5—Absorption Curves for 1,4-Bis-*p*-dimethylsulphamoylbenzamidoanthraquinone (III)

solution at the boil can the stable colloidal solution corresponding to the soaped colour be obtained directly, although it is also produced by heating the cold solution (Fig. 5).

It was thus possible to show that a process analogous to that occurring on soaping can take place also in the absence of a substrate. The stabilising action of the substrate on the unsoaped form can be seen from the fact that the direct transition from the reduced state to the soaped form is not possible with dyeings, but can be carried out in substance.

It has not yet been possible to isolate the dyes in a pure and unchanged form from the colloidal solution, so it is uncertain whether they are in an amorphous or a microcrystalline form.

## 11. CRYSTALLINE MODIFICATIONS OF A DYE

Like azoic pigments, phthalocyanines, and other dyes, certain vat dyes are known in different crystalline modifications or polymorphic forms. In spite of identical chemical composition, these modifications differ markedly in various physical properties, e.g. colour, melting point, X-ray diagram, and infrared and visible absorption spectrum.

M. Stäuble was the first to show clearly that there is a connection between such modification of a dye and the colours of the unsoaped and soaped dyeings<sup>15</sup>. He succeeded in producing two physically different forms of 1-*p*-dimethylsulphamoylbenzamido-4-benzamidoanthraquinone (II), the shades of which corresponded to those of the unsoaped and soaped dyeings (Fig. 6).

The metastable  $\alpha$ -modification of this dye is obtained by dissolving it in 80% sulphuric acid and precipitating in microcrystalline form by addition of ice. Like the unsoaped dyeing it is reddish brown, with an absorption maximum at 496 mμ.

If the  $\alpha$ -modification is boiled in aqueous suspension, it is converted to the stable  $\beta$ -form, and this can occur even on milling, or on drying if it is not carried out carefully at room temperature. The transition to the  $\beta$ -form can be produced also by gently grinding with alcohol and similar solvents. If the  $\alpha$ -form is precipitated as coarse crystals, e.g. by allowing a sulphuric-acid solution of the dye to stand, the transformation is much more difficult. It has not yet been clearly established whether, in this case, another polymorphic form is present. The  $\beta$ -form is obtained by recrystallising the dye from organic solvents. It has the brilliant red colour and the absorption spectrum with a double maximum characteristic of the soaped dyeing. By redissolving in sulphuric acid it can be reconverted to the  $\alpha$ -form. The two modifications differ also in their X-ray diagrams (Fig. 7) and their infrared spectra.

Other homologues, e.g. III, which are more difficult to develop by soaping, give a correspondingly more stable  $\alpha$ -form, which is not changed by boiling the aqueous dispersion (Fig. 8). Such forms can be ground wet without suffering any change, and in consequence it is possible by mass coloration with the  $\alpha$ - and the  $\beta$ -pigment respectively to produce viscose corresponding to the

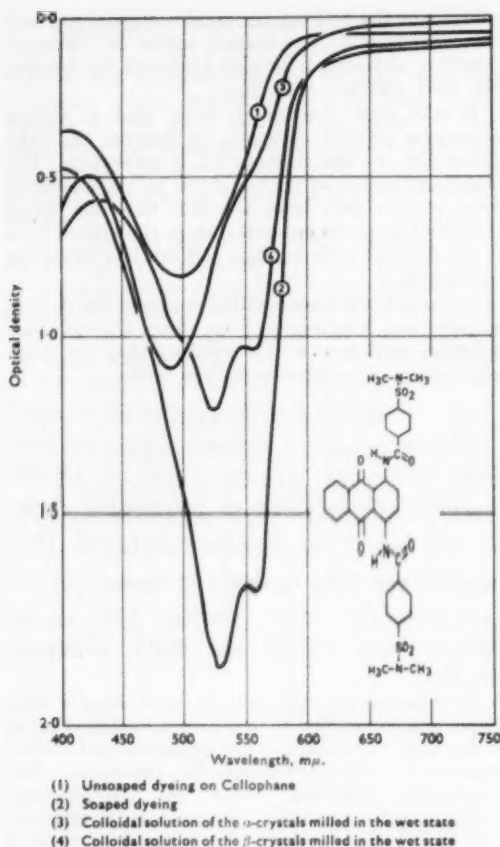


FIG. 8—Absorption Curves for 1,4-bis-p-dimethylsulphamoylbenzamidoanthraquinone (III)

unsoaped and the soaped colours (Fig. 9). Neither of these is affected by soaping at the boil. Only by previous vatting and reoxidation in the fibre is it possible to change the viscose with the  $\alpha$ -pigment into the brilliant red of the  $\beta$ -form by subsequent soaping.

The results obtained by M. Stäuble provided the complete experimental proof that the differences in colour between unsoaped and soaped dyeings cannot be due to transition from the molecular to the crystalline state, as both forms can be isolated as well-defined crystalline modifications.

The gap left by the experiments with colloidal solutions was thereby closed. But there still remained the possibility that, although the colour change is not a consequence of crystallisation on soaping, single adsorbed molecules corresponding to the  $\alpha$ -form might be transformed into crystals of the  $\beta$ -modification.

## 12. DICHOISM OF CRYSTALS AND DYEINGS

The unsoaped dyeing of the dimethylsulphamoyl derivative (II) shows negative dichroism, whilst the  $\alpha$ -crystals, with reference to the long axis of the needles, show slight positive dichroism. It follows that the molecules must be oriented in the crystal with their oscillation system parallel to its long axis, for the anisotropy of the crystal depends on the anisotropy of the individual molecules<sup>16</sup>. This gives no information about the position of the molecules in relation to their constitution, so long

as the direction of oscillation cannot be related to the constitutional formula.

On soaping, the dichroism of the dyeing changed from negative to positive, irrespective of whether the soaping was carried out for 60 sec. or 6 hr. (Fig. 10). The possibility that all the molecules had undergone a rotation through 90° can be excluded from the start. The positive dichroism is due either to a change in the oscillation system in the dye molecule or to the formation of micro-crystalline needles having positive dichroism. The  $\beta$ -form is in fact strongly anisotropic, and if a suitable solvent is chosen, e.g. benzene, it can be obtained in needles, whilst under normal conditions it crystallises in the form of leaflets. These needles, however, show a dichroism which, relative to their length, gives a change from full colour to colourless within an angle of about 45° (Fig. 11). If crystalline needles were in the fibre, their dichroism should mutually cancel out, and the dyeing should not show any dichroism, because they would be fixed only in the direction of the fibre axis, not at an angle to it. It follows that the positive dichroism of the soaped dyeing must be a property of the molecules.

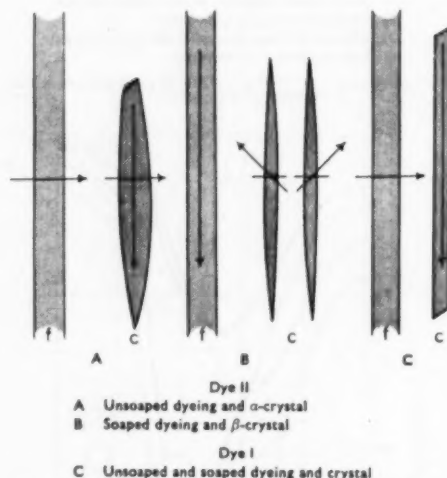


FIG. 11—Dichroism of the Crystal (c) and the Dyeing (f) (arrow indicates position of the light vector when full colour appears)

This result is of particular importance because it shows that oriented dye molecules are adsorbed on the fibre both before and after soaping. Moreover, it raises the question as to whether  $\alpha$ - and  $\beta$ -modifications are polymorphic forms at all, or whether they should be called desmotropic modifications, i.e. isomers<sup>17</sup>. It is hoped to revert to this interesting question in some future work.

Although the dimethylsulphamoyl derivative (II) shows agreement between the shade and the absorption spectra for the dye crystal and the soaped dyeing, this is certainly not the case with 1,4-dibenzamidoanthraquinone (I). The soaped dyeing shows negative dichroism (II colourless, I reddish orange), whereas the crystal needles show positive dichroism (II red, I pale yellow). Most of the crystals, especially the bigger ones, show no



(1) II  $\alpha$ -form  
(2) II  $\beta$ -form

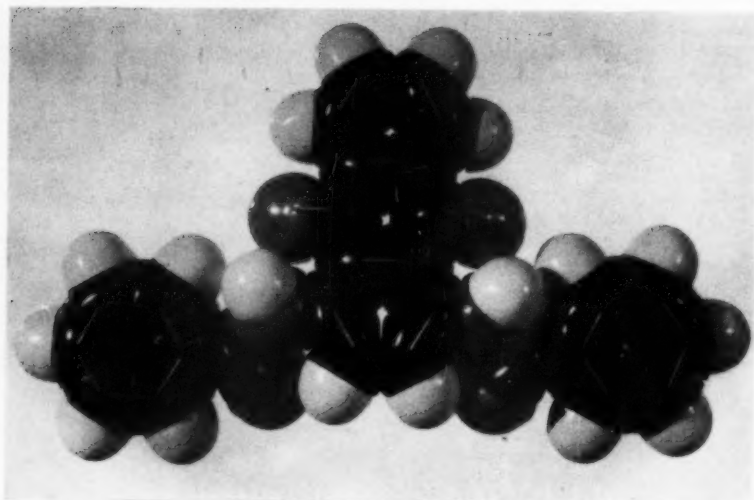


(3) IX  $\alpha$ -form  
(4) IX  $\beta$ -form

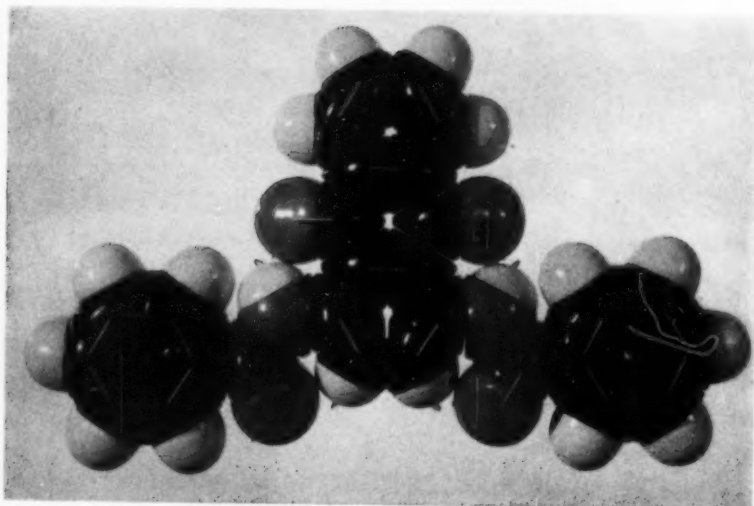


(5) III  $\alpha$ -form  
(6) III  $\beta$ -form

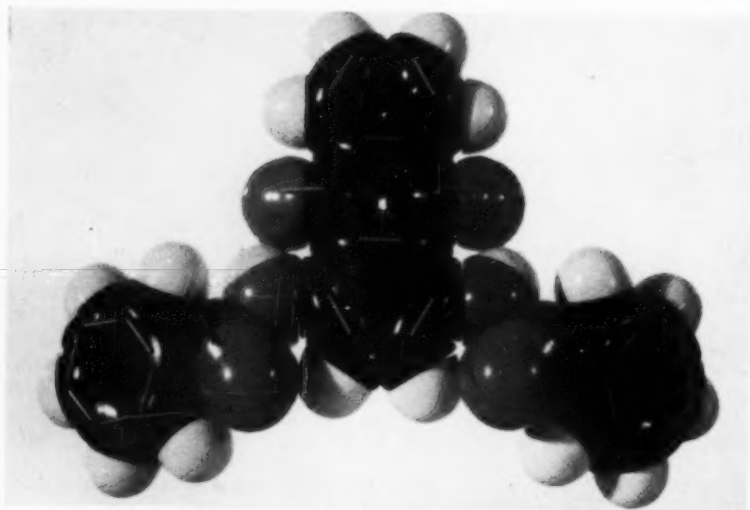
FIG. 7—X-Ray Diagrams of Dyes II, III, and XI



$\alpha_2$  form



$\beta_1$  form



$\beta_2$  form

FIG. 31—Stuart-Briegleb Molecular Models of the Postulated  $\alpha_2$ ,  $\beta_1$ , and  $\beta_2$  Structures



dichroism at all, probably on account of the formation of twin crystals. Only one crystalline modification of this dye is known. From it a colloidal form of particle size about  $0.1 \mu$  was produced by milling. The absorption spectrum of the latter is different from that of the soaped dyeing, which is identical with that of the colloidal solution obtained from the vat (Fig. 12). It follows that in the crystal there must be some sort of interaction among the molecules, which is not found either in the soaped form or in the colloidal solution of the reoxidised dye.

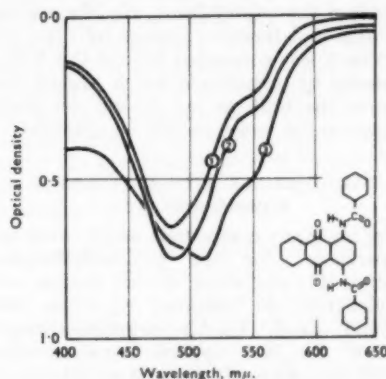


FIG. 12—Absorption Curves for 1,4-Dibenzamidoanthraquinone (I)

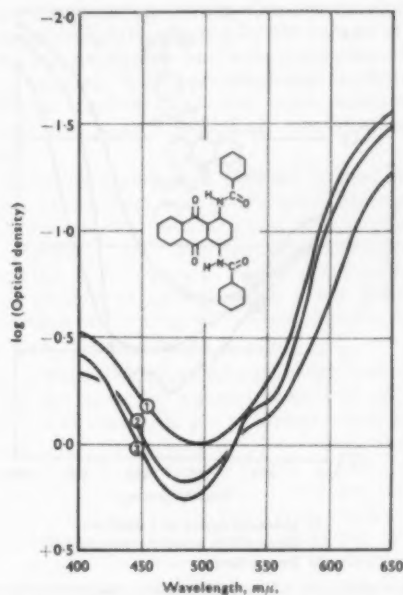
In the first example above it would be possible to argue that the growth of the crystal needles in the fibre could occur in another direction, leading to positive dichroism, but this possibility also is excluded here. The dichroism of the dyeing can be ascribed only to the adsorbed molecules, which, however, does not exclude the presence of well-defined adsorbed multimers, e.g. double molecules with both halves having the same direction of oscillation.

### 13. DIFFERENT COLOURS FROM DIFFERENT DEVELOPING AGENTS

As is well known, vat dyeings can be stripped completely by means of certain organic solvents at the boiling point, whilst the same treatment at room temperature normally has no effect. If, however, wet unsoaped dyeings are placed in a polar solvent, a change of colour to that of the soaped dyeing occurs even at room temperature, but, depending on dye and solvent, other colours may be observed as well. This behaviour may be illustrated by the following typical examples—

1,4-Dibenzamidoanthraquinone (I) gives on soaping a somewhat yellowish red, whilst an aqueous-alcoholic solution of ethylene chloride produces a fairly bluish, dichroic colour, which is unstable and is changed, e.g. by soaping at the boil, irrespective of the nature of the substrate, to the soaped colour (Fig. 13).

The *p*-methoxy derivative (VIII), however, which is normally developed to a dichroic reddish

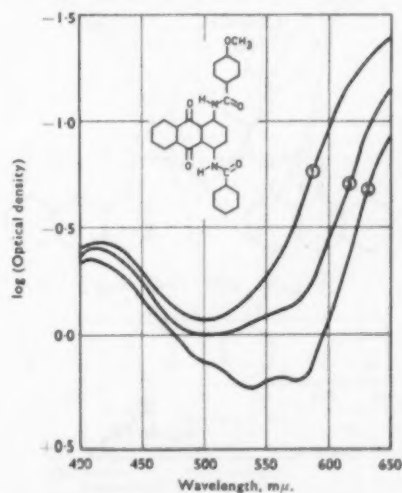


(1) Unsoaped dyeing on Cellophane  
(2) Developed with ethylene chloride in aqueous alcohol  
(3) Soaped dyeing

FIG. 13—Absorption Curves for 1,4-Dibenzamidoanthraquinone (I)

violet with one absorption maximum, yields a positively dichroic blue-violet of greater intensity having a double maximum (Fig. 14). This form is the more stable one, as it is not affected by boiling soap solution. Starting from the soaped colour, the bluish violet cannot be obtained.

With the *p*-dimethylsulphamoyl derivative (II) the change from orange-brown to brilliant red occurs with some solvents, e.g. ethylene chloride, via a violet intermediate stage. With other solvents, e.g. benzyl alcohol, the development stops



(1) Unsoaped dyeing on Cellophane  
(2) Developed with ethylene chloride in aqueous alcohol  
(3) Soaped dyeing

FIG. 14—Absorption Curves for 1-p-Methoxybenzamido-4-benzamidoanthraquinone (VIII)

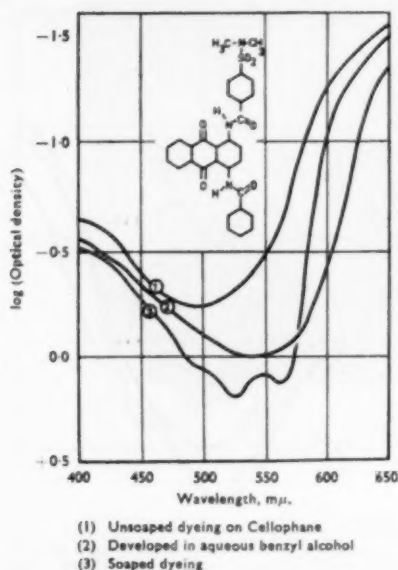


FIG. 15—Absorption Curves for 1-*p*-Dimethylsulphamoylbenzamido-4-benzamidoanthraquinone (II)

at the violet stage, which has only one absorption maximum and is dichroic (Fig. 15). Boiling soap solution converts the violet, though much more slowly than the unsoaped form, into the stable, brilliant red form. On Cellophane this change occurs much more easily than on cotton.

With the *p*-chloro-*p*-dimethylsulphamoyl derivative (IX) the violet, once formed, is so stable that the change to the brilliant red form is no longer possible on cotton except after revatting, reoxidising, and soaping. It has not yet proved possible to produce this violet form out of contact with the fibre.

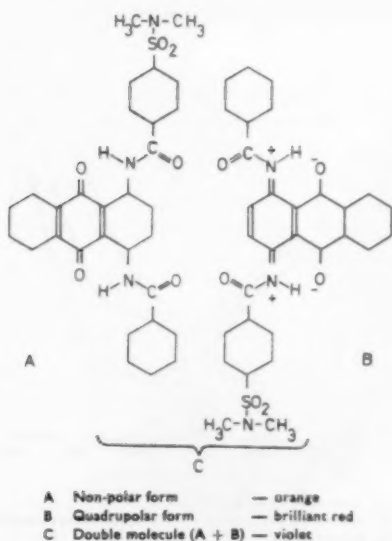


FIG. 16—1-*p*-Dimethylsulphamoylbenzamido-4-benzamidoanthraquinone (II)

As, in accordance with the working hypothesis, the non-polar structure was ascribed to the unsoaped  $\alpha$ -form, and the quadrupolar, doubly ionic structure to the soaped  $\beta$ -form, the violet form was assigned the singly ionic, dipolar structure. This last could arise if one non-polar  $\alpha$ -molecule (A) and one quadrupolar  $\beta$ -molecule (B) form a double molecule of the type of quinhydrone, which would result in one ionic group per molecule (Fig. 16). That the violet form is not resistant to various influences, and e.g. on boiling with soap solution gradually changes to the brilliant red form, is attributed to the fact that at least half of the quinhydrone, viz. the  $\alpha$ -molecule, is unstable and tends to change into the  $\beta$ -form. From this it was concluded that, if this half could be replaced by a molecule which cannot possibly change to the brilliant red  $\beta$ -form, an analogous but more stable violet should be obtained.

#### 14. DYEINGS WITH MIXTURES OF HOMOLOGOUS DYES

There are many compounds which could be used as "partners" for the *p*-dimethylsulphamoyl derivative (II) and which do not change, or only insignificantly, on soaping, e.g. the primary compound itself, 1,4-dibenzamidoanthraquinone (I). This dye was applied together with the *p*-dimethylsulphamoyl derivative (II) in equimolecular proportion. The unsoaped dyeing did not show any great difference compared with the dyeings of the single components. On soaping, however, a violet was obtained instead of the brownish red to be expected from the single components (Fig. 17). As assumed, the colour proved to be stable, even to prolonged soaping at the boil, but not to strong alkalis. Similar behaviour is shown by IX.

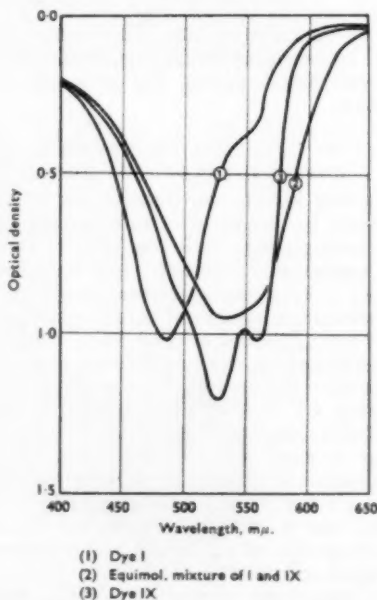


FIG. 18—Absorption Curves for Soaped Dyeings on Cellophane

The relation of this violet to that obtained by selective development of the homogeneous *p*-dimethylsulphamoyl derivative (II) is obvious. Like the latter, it is dichroic and has an absorption spectrum with a single maximum (Fig. 18).

A still more striking result is obtained if the *o*-chloro-*p*-dimethylsulphamoyl derivative (X) is used in the mixture. The brilliant red  $\beta$ -form cannot be formed with this dye, owing to the substitution of chlorine in the *ortho* position. Nevertheless this combination leads, again, to a violet (Fig. 19).

A more detailed investigation of the possible effects of homologous dyes of the 1,4-dibenzamidoanthraquinone series has shown that very different types of interaction can occur. These violets are not limited to 1:1 stoichiometric proportions of the dye molecules in the fibre (Fig. 19). The actual behaviour is more complex than was assumed in the hypothesis outlined above. Nevertheless, the hypothesis has the merit of having helped to uncover this problem.

#### 15. MIXTURES OF HOMOLOGOUS DYES IN SUBSTANCE

Whilst it was not possible with the *p*-dimethylsulphamoyl derivative (II) alone to isolate the violet form in substance, in the mixture with 1,4-dibenzamidoanthraquinone (I) it can be isolated as a further modification, which shows its much greater stability, as could be observed with the dyeing as well.

The violet form can be obtained, in a similar manner to the  $\beta$ -form<sup>15</sup>, by reprecipitating the two components together and grinding the resulting  $\alpha$ -form with alcohol. The same result is obtained by revatting the components together, and, depending on the method of oxidation, the violet form may be produced directly. Separate reprecipitation, revatting, and also recrystallisation, on the other hand, lead only to a mechanical mixture of the two dyes. It follows that the violet modification must already be formed within the  $\alpha$ -form, and its decay, e.g. on trying to recrystallise it, is irreversible; i.e. it is necessary to reprecipitate from sulphuric acid or from the vat to obtain it again.

As recrystallisation is not immediately possible, it is certainly not simple to obtain this substance in a pure state. It is very difficult to detect or to exclude the presence of small amounts of the single components, so no information is given on its composition. However, the stability of these preparations is so good that the violet form from the mixture of 1,4-dibenzamidoanthraquinone with the *p*-chloro-*p*-dimethylsulphamoyl derivative (IX) can be milled and used, e.g. for the mass coloration of viscose.

#### 16. COLOUR CHANGES IN ORGANIC SOLUTIONS OF DYES

All the dyes of the 1,4-dibenzamidoanthraquinone series investigated, when dissolved in organic solvents, showed only slightly different colours, which normally corresponded or were very similar to those of the unsoaped dyeings. They

have an absorption spectrum with one maximum, and are only slightly affected by the nature of the solvent, i.e. practically no solvatochromic effect can be observed. With dyes which can be obtained in different modifications, the same solution is produced irrespective of which modification is dissolved.

As shown for Indanthren Brilliant Scarlet RK<sup>4</sup>, a scarlet polar form can be obtained in organic solvents by addition of methanolic caustic potash. After distilling off the alcohol, the dye is precipitated as a blue salt, which gives again in benzene-alcohol or alcohol alone a red solution. But washing or diluting with water at once yields the original yellow-orange solution.

Dyes of the 1,4-dibenzamidoanthraquinone series are also polarised by caustic potash in methyl alcohol, and violet-reds are produced which have, however, only one absorption maximum, and do not correspond to the soaped colour. After a short time these colour changes, which continue slowly, are no longer reversible, as the dye in the solution is gradually saponified. This sensitivity of the amide groups indicates that the molecules in solution are not stabilised by intramolecular hydrogen bonds.

Of special interest in this connection is the mixture of 1,4-dibenzamidoanthraquinone (I) with the *p*-dimethylsulphamoyl derivative (II), for its  $\alpha$ -form dissolves in benzene with an orange colour corresponding to that of the unsoaped dyeing, and on addition of methanolic caustic potash gives the violet colour of the soaped dyeing with the same absorption spectrum (Fig. 20). However, if the  $\alpha$ -form is dissolved in alcohol, a violet solution which corresponds to the benzene solution after addition of the caustic potash is obtained directly.

It follows that this mixture is very easily polarised, so the dipole moment of the alcohol is

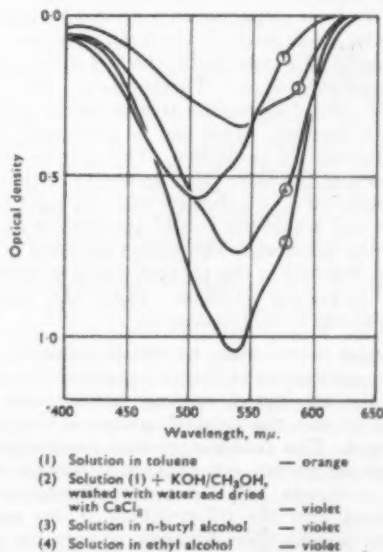


FIG. 20—Absorption Curves for Equimol. Mixture of I and II recrystallised from 80% H<sub>2</sub>SO<sub>4</sub>.

already great enough. The specific effect of the alcohol indicates, however, that the molecules of the solvent have a stabilising influence similar to that of the cellulose in the case of the dyeing. This solvatochromic phenomenon is not directly connected with the dipole moment of the solvent.

These experiments prove that the violet form, too, is not bound up with the solid state, but is of molecular nature. But they cannot show whether multimerism or structural isomerism is involved. It is certain that neither mesomeric forms nor equilibrium isomers can be present, because the colour of the solution is either orange or violet.

#### 17. CONSTITUTION AND POSITION OF THE MOLECULES IN THE FIBRE

So far there have been some indications of the direction of oscillation of the dye molecules, e.g. with reference to the fibre axis, but still unrelated to the molecular structure itself. In order to obtain a clear picture it is best to start from the vat and to study the different stages of the dyeing one after the other—

##### (a) Reduced State

If the absorption spectra of a reduced dye in solution and on the fibre are compared, they are usually found to be almost identical, but with the spectrum of the dyeing shifted a little towards longer wavelengths. An analogous behaviour is observed with direct dyes, and is explained by the adsorption of the dye molecules by the fibre substance.

Like direct dyes, vat dyes arrange themselves with the molecular axis, which corresponds to the main direction of electronic oscillation, parallel to the fibre. In consequence they show positive dichroism. But whilst direct dyes in general have only one direction of oscillation, reduced vat dyes have in many cases a branched electronic system, and there is in consequence a second direction of oscillation, at an angle to the main direction. This is normally the case with the 1,4-dibenzamido-anthraquinone dyes. Furthermore, the leuco forms of these dyes possess an absorption spectrum with two maxima, which can be attributed to the two directions of oscillation. This can be verified by observing the absorption spectrum of the leuco form adsorbed on a substrate with the light vector parallel and transverse to the direction of orientation of the substrate. The main maximum is most strongly marked in the parallel position, and least in the transverse position, whilst the converse applies to the second maximum.

In order to ascertain to which molecular axes the two oscillations of the two absorption maxima are to be attributed, various substituents were introduced into the benzoyl groups of the parent compound. This causes a gradual displacement of the main maximum, but scarcely affects the short-wave maximum. If, however, substituents are introduced into the 6,7-positions of the anthraquinone nucleus, then, in contrast, only the short-wave maximum is displaced, and the main maximum only slightly altered (Fig. 21).

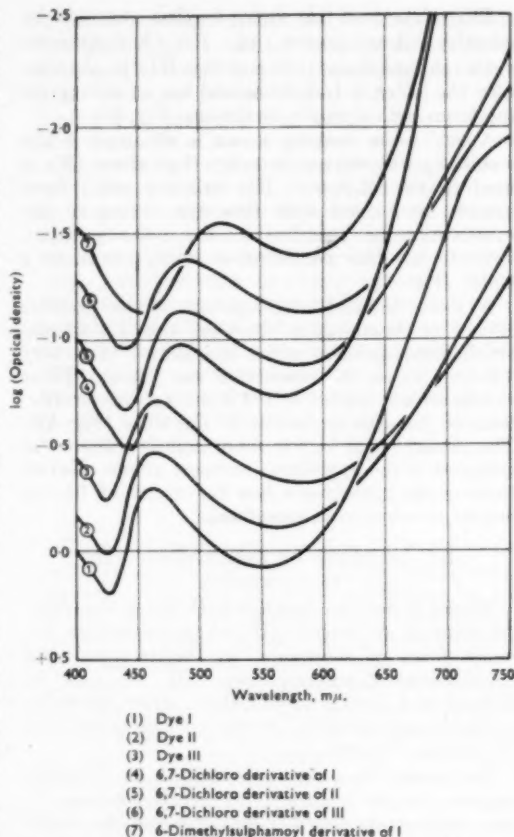


Fig. 21—Absorption Curves illustrating Colour of Reduced Vat Dyes

It follows that the molecules are adsorbed with the axis of the benzamido groups, which corresponds to the main maximum, parallel to the fibre; whilst the anthraquinone nucleus, to which the short-wave maximum is attributable, lies across it.

The question whether the leuco form is adsorbed in the amide (A) or in the iminol (B) form, which is of interest also in connection with the substantivity of azo dyes, has been investigated with the aid of suitable homologous compounds, firstly mono- and di-*N*-methyl-1,4-dibenzamido-anthraquinone (D) (Fig. 22). Both dyes are only pale yellow and have an orange-yellow vat: they possess no substantivity. The iminol cannot be formed in this case, but the lack of substantivity may be due to prevention of coplanarity, so 1,4-dibenzamido-2,3-dibromoanthraquinone (E) was investigated. This may have either an amide or an iminol structure, but it cannot be planar: it, too, possesses no substantivity. It is very difficult to reduce, forming a vat only in the presence of dimethylformamide, and has, as was to be expected, a yellow leuco form. The deep colour, ranging from carmine to blue-green, of the leuco forms of the 1,4-dibenzamidoanthraquinones implies that they must be coplanar, because only then is the electron oscillation along the axis of the benzoyl groups possible.



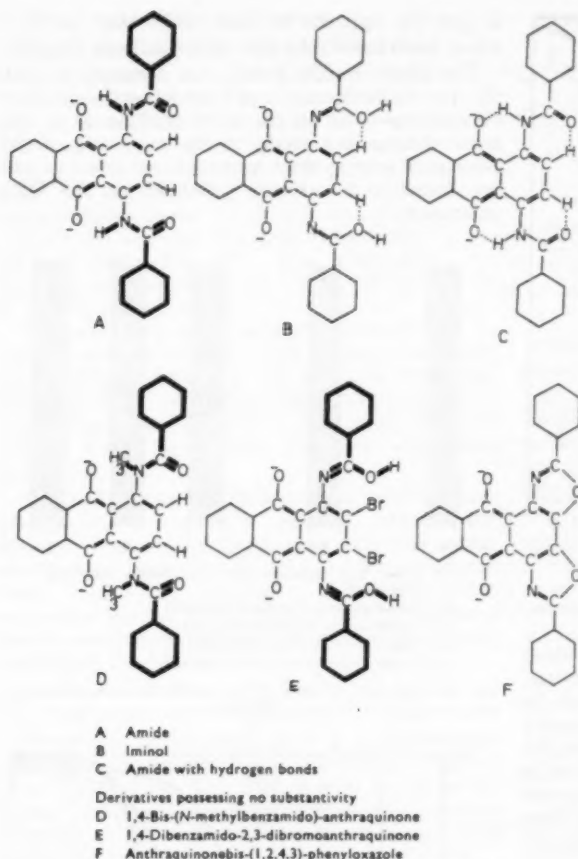


FIG. 22—Possible Structures of the Leuco Form of 1,4-Dibenzamidoanthraquinone (I)

Coplanarity alone is not sufficient if a strong resonance system cannot be formed, a point which is confirmed by the anthraquinone-bisoxazole (F), which in spite of a completely planar structure forms only a yellow vat without any substantivity. The removal of the two hydrogen atoms therefore results in a marked decrease in conjugation, although at first sight the conjugated system is very similar to that of the hypothetical iminol form of 1,4-dibenzamidoanthraquinone.

The resonance depends mainly on the possibility of a prototropic shift of the negative charge to the oxygen atoms of the amide groups, which is impossible in the oxazole (Fig. 23). In consequence,

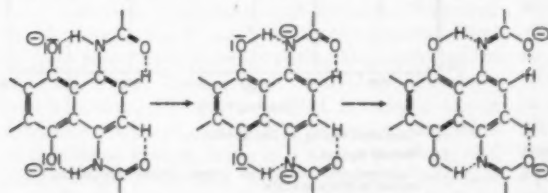


FIG. 23—Possible Shift of the Negative Charge to the Carbonyl Groups of the Amide Residues in the Leuco Form of 1,4-Dibenzamidoanthraquinone

all the vat acids of the 1,4-bisaroilamino-anthraquinones are all yellow to orange. A carbonyl group, however, can take over a negative charge, but not a hydroxyl, from which it must be concluded that the amide structure is the most probable for the leuco form.

Both amide and iminol forms can, for steric reasons, only be coplanar if hydrogen bonds are formed with the hydrogen atoms of the anthraquinone nucleus. It follows that the most probable structure is a coplanar amide form stabilised with hydrogen bonds (C).

The postulation of such hydrogen bonds is, as far as is known, new for dyes, but the possible existence of such hydrogen bonds is already known in organic chemistry<sup>18</sup>.

In contrast to what is stated by the authors referred to above, it seems more probable that, with 2-hydroxy- and 2,2'-dihydroxydiphenyl, the protons come from the nucleus rather than from the hydroxyl groups, thus bringing about stabilisation of the energetically-favoured planar configuration. This is confirmed by observations made with molecular models.

What was still required was an example to show that coplanarity without the possibility of tautomerisation of the amide form is in fact sufficient for substantivity. Such an example was found in 1,4-dithiazolylaminoanthraquinone (Fig. 24). The dye is blue and exhausts much less readily from its red-orange vat than 1,4-dibenzamidoanthraquinone, which has a carmine vat. Coplanarity is sterically possible only if the thiazole nitrogen and not the sulphur is oriented towards the anthraquinone nucleus. A hydrogen bond is required, too, for coplanarity, but is in this case presumably much weaker.

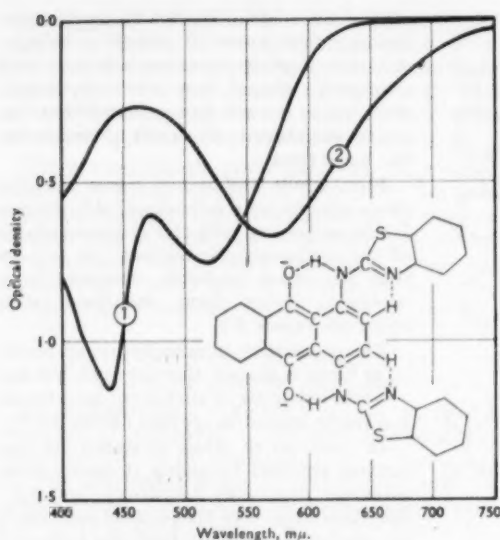
The underlying resonance structure is very similar to that of 1,4-dibenzamidoanthraquinone (I), but tautomerisation, in view of the aromatic character of the thiazole ring and the postulation of mesomerism in its direction, is inconceivable.

In contrast to the benzoylated dye, this derivative has a markedly dichroic vat (II red, I orange) and a weaker resonance system in the direction of the thiazole groups, as their coplanar position is less stabilised and any shift of the negative charge to the nitrogen of the thiazole group is improbable. In consequence the main maximum, compared with the second maximum, is much less pronounced. The leuco form is only orange and much less substantive than that of 1,4-dibenzamidoanthraquinone. The behaviour of this apparently unrelated dye thus confirms the above assumption that not only coplanarity, but also the amide form is essential for the vat (Fig. 25).

#### (b) State after Reoxidation

In the unsoaped dyeing the state of the molecules cannot be unambiguously defined





(1) Leuco form in solution  
(2) Alkaline colloidal solution of the reoxidised dye

FIG. 24—Absorption Curves for 1,4-Dithiazolylaminoanthraquinone

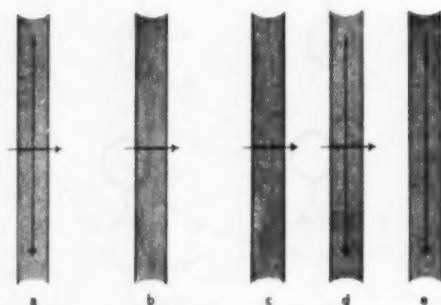
in many cases. From the moment of reoxidation through the rinsing and neutralisation to the drying, continuous changes may occur which cannot be halted. Obviously, reoxidation must not be carried out in hot solution if a partial transition to the soaped colour is to be avoided with certainty, and in extreme cases the colour obtained may even depend on the conditions of reoxidation. Although these differences are as a rule only small, they can become very marked after subsequent soaping.

All the 1,4-dibenzamidoanthraquinone dyes investigated, with one exception, show negative dichroism immediately after reoxidation. The colours vary only a little between brownish orange and reddish brown, and are relatively dull and weak. Some derivatives show on drying a decrease in the negative dichroism; others show weak colour dichroism. How far disorientation of the adsorbed molecules or changes in the electronic oscillation are responsible cannot be decided for the present.

It seems clear that the change from the positive dichroism of the leuco form to the negative dichroism of the reoxidised form cannot be due to rotation of all the molecules through  $90^\circ$ . Rather it must be assumed that the re-formation of the quinonoid structure inhibits the oscillation in the direction of the benzamido group, and only the transverse oscillation, which is present though very weak in the leuco form, can take place. This would mean that the benzoyl groups contribute practically nothing to the resonance of the reoxidised form, as is the case with the organic-solvent solutions of the dyes. In fact it can be shown that substituents in the 6,7-positions of the anthraquinone nucleus do shift the absorption maximum of the reoxidised form, whilst substituents in the benzoyl groups have hardly any effect. Groups in the *ortho* position, which are able to affect the transverse oscillation system, form an exception; their effect

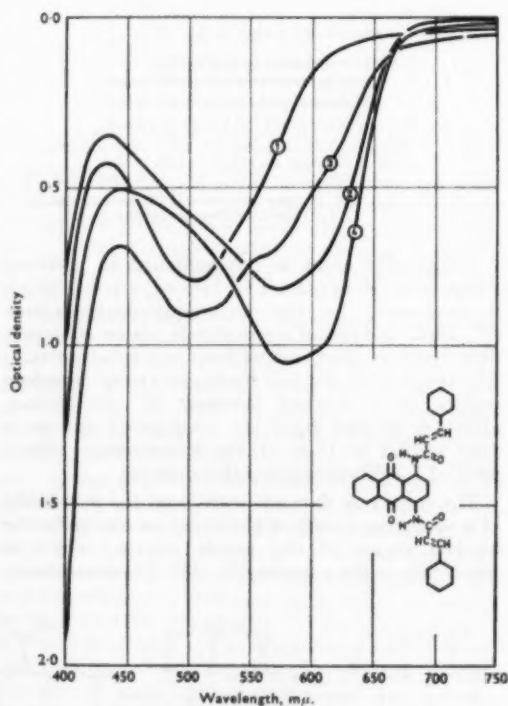
is just the opposite to that which they produce when introduced into the anthraquinone nucleus.

The above results justify the assumption that the dye molecules are—at least immediately after reoxidation—still in the same position as in the reduced form, but owing to the weakening of the resonance system they have a lower affinity, and are therefore less firmly adsorbed on the fibre substance.



(a) Leuco form (positive dichroism, feeble transverse oscillation)  
(b) Unsoaped dyeing (negative dichroism)  
(c) Soaped dyeing (negative dichroism)  
(d) Soaped dyeing (colour dichroism)  
(e) Soaped dyeing (positive dichroism)

FIG. 26—Dichroism of Dyes of the 1,4-Dibenzamidoanthraquinone (I) type



(1) Unsoaped dyeing on Cellophane  
(2) Soaped dyeing  
(3) Colloidal solution of the orange crystal modification milled in the wet state  
(4) Colloidal solution of the violet crystal modification milled in the wet state

FIG. 27—Absorption Curves for 1,4-Dicinnamidoanthraquinone (XI)

## (c) State after Soaping

Whilst the behaviour of the different dyes so far is quite similar, marked differences are observed on soaping. Three groups of dyes can be distinguished, the first comprising those with pronounced negative dichroism (Fig. 26). The change in colour may be either small and hypsochromic, as with 1,4-dibenzamidoanthraquinone (I) or large and bathochromic, as with the 1,4-dicinnamidoanthraquinone (XI) (Fig. 27). The absorption spectrum has one maximum and an inflection in the long-wave region.

A second group comprises those dyes which show "colour dichroism" after soaping, i.e. which show different colours in the two directions, e.g. the *p*-methoxy derivative (VIII). The change is always bathochromic, and in most cases produces violets, which again have only one absorption maximum.

A third group comprises dyes which show positive dichroism after soaping. Again, the change is always bathochromic, but this group contains a wide range of bright and strong colours from scarlet to blue-violet. The absorption maximum is split into a more or less pronounced double maximum, the long-wave maximum being somewhat the weaker.

## 18. DISCUSSION AND INTERPRETATION OF RESULTS

There can be no question of a comprehensive theoretical treatment even of the narrow range of dyes investigated, but first it will be useful to review existing knowledge about the relation between colour and constitution as far as it is applicable to these dyes.

Allen *et al.*<sup>19</sup> have shown that with anthraquinone derivatives the colour depends on the possibility of substituents acting as electron donors to the nucleus and especially to the carbonyl groups. The resulting ionic limiting structures are to be regarded as the most important resonance forms. These authors were also the first to describe the occurrence of a characteristic double maximum with 1,4-diaminoanthraquinone, and interpreted it as a result of the twofold mesomeric shift of electrons from the amino to the carbonyl groups.

Peters and Sumner<sup>20</sup> state that with 1,4-derivatives the two chromophoric systems may interact with formation of a new system, which produces a double maximum. Flett<sup>21</sup> showed by infrared measurements that the weakening of the carbonyl frequency with 1,4-diaminoanthraquinone cannot be due to hydrogen bonds but must be the consequence of a strong predominance of the ionic structure. Sheppard and Newsome<sup>22</sup> showed that hydrogen bonds can bring about a stabilisation of polar structures, thus favouring the contribution of such forms to the ground state. On steric grounds alone the formation of hydrogen bonds with the carbonyl groups is a necessary condition of the amino groups being in a planar position, and mesomerism with the ionic structures becomes possible via resonance forms of the amide type (Fig. 28).

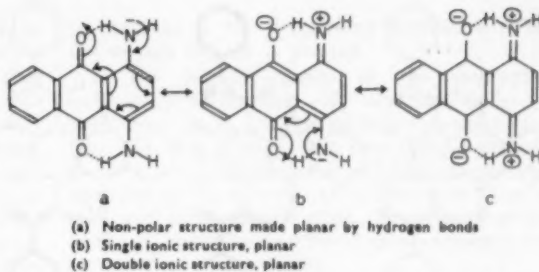
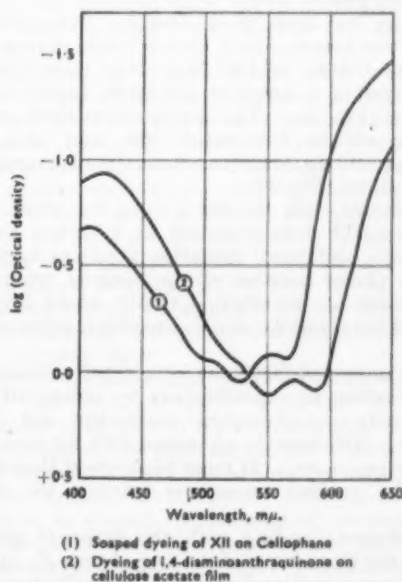


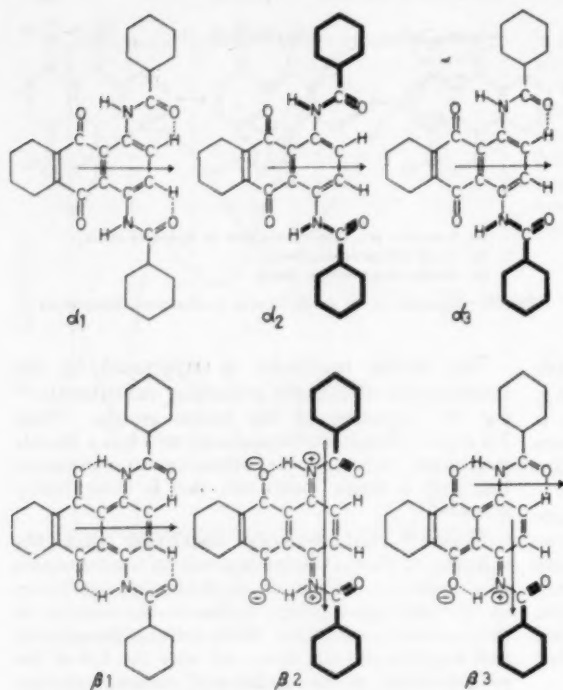
FIG. 28—Resonance of the Amide Type in 1,4-Diaminoanthraquinone

The double maximum is suppressed by the introduction of electron-attracting substituents<sup>20</sup>, e.g. by acylation of the amino groups. Thus, 1,4-diphenylaminoanthraquinone still has a double maximum, whereas the dibenzamido compound has only a single maximum and is more feebly coloured.

Merian<sup>23</sup> has recently confirmed that the splitting of the maximum depends on the formation of a double ionic form, in which the two oscillators in the molecule coalesce, rather in the manner of two coupled pendulums. With both anthraquinone and naphthaquinone dyes, not only the 1,4 or the *para* position of the amino and carbonyl groups, but also a "cross-wise" orientation can produce a double maximum if steric conditions permit. However, it is quite possible for such structures to be stabilised by hydrogen bonds without any appearance of a double maximum.

Summing up, it is seen that the resonance system of 1,4-diaminoanthraquinone with the double maximum depends on the great contribution of the double ionic structure. This mesomeric system is

FIG. 29—Absorption Curves for 1-*p*-Dimethylsulphamoylbenzamido-4-*p*-methylbenzamido-6-chloroanthraquinone (XII) and 1,4-Diaminoanthraquinone



Arrows indicate direction of electronic oscillation  
Parts of the molecules not lying in the plane of the paper are shown in bold lines

FIG. 30—Possible Structures for the Unsoaped ( $\alpha$ ) and Soaped ( $\beta$ ) State (cf. Fig. 31)

suppressed by electron-attracting groups, which implies that these groups can lie in the same plane as the remainder of the system, as otherwise a mesomeric displacement of electrons to the amide carbonyl groups would be impossible.

Among vat dyes themselves are those which, even after soaping, have only a single maximum, whereas others, which have lost their double maximum as a result of acylation, regain it on soaping (Fig. 29). The purely theoretical possibilities will be formulated first, and then an attempt will be made to relate the experimental observations (Fig. 30).

Beginning with the leuco dyes, for which the planar amide form stabilised by hydrogen bonds has been confirmed, oxidation produces first  $\alpha_1$ . If the planar position of the benzoyl groups is simultaneously disturbed,  $\alpha_2$  results, whilst disturbance of the planarity on only one side is represented by  $\alpha_3$ .

The unsoaped forms are very readily reducible, are sensitive to saponification by strong alkalis, have only one absorption maximum, and show negative dichroism, in agreement with the formulae chosen ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ). It must be assumed that there may be gradual transitions between the three forms.

Hydrogen bonding with the carbonyl groups yields the three forms of the soaped state  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , which are correspondingly more difficult to reduce and less sensitive to strong alkalis. In  $\beta_1$  the benzoyl groups, thanks to their planar position,

take part in mesomerism, which must lead to oscillation in the direction of the anthraquinone nucleus and hence to negative dichroism. This is not the case with  $\beta_2$ , so that here the typical resonance system of 1,4-diaminoanthraquinone can be established, and positive dichroism results. In  $\beta_3$  both types are combined, and therefore colour dichroism occurs. This scheme is in conformity with the three types of product, differing in dichroism, obtained on soaping (Fig. 31).

With 1,4-dibenzamidoanthraquinone (I) a transition from  $\alpha_1$  to  $\beta_1$  may be assumed. The dyeing is more difficult to reduce and less sensitive to alkali, but the electrophilic benzoyl groups still take part in mesomerism, and an increased negative dichroism and a small hypsochromic shift in colour result (Fig. 32).

With 1,4-dicinnamidoanthraquinone (XI), too, a transition from  $\alpha_1$  to  $\beta_1$  must be assumed. The dyeing shows a great change in colour from brown-red to blue-violet, but continues to show negative dichroism. The electron-attractive effect of the acyl group is greatly increased, which leads to a correspondingly strong transverse resonance if complete planarity is produced by hydrogen-bond formation. *p*-Iodobenzoyl groups give a similar effect. It follows that the  $\beta_1$  state, too, is strongly polarisable, but in a different direction from the  $\beta_2$  form.

If 1,4-dibenzamidoanthraquinone (I) is developed with ethylene chloride, a more bluish, colour-dichroic, but unstable form is obtained, to which structure  $\beta_3$  can be ascribed (Fig. 13). One benzoyl group must have been rotated out of the plane, and therefore does not contribute to the resonance system. This state seems to be the stable one with 1-*p*-methoxybenzamido-4-benzamidoanthraquinone (VIII), for on soaping a colour-dichroic reddish violet results (Fig. 14). Ethylene chloride is evidently able in this case to release both benzoyl groups from the plane, so that a transition from  $\alpha_2$  to  $\beta_2$  occurs. The dyeing shows positive dichroism, has a double maximum, and is very stable.

The peculiar behaviour of *p*-chlorobenzamido-4-benzamido-7-chloroanthraquinone (VI), again, fits well into the scheme (Fig. 2). After oxidation the dye is first converted into the  $\alpha_2$  form, so that, if soaping is carried out immediately, a bluish violet showing positive dichroism and with a double maximum results ( $\beta_2$ ). If the dyeing is first dried, stabilisation of the unsoaped form, producing  $\alpha_3$ , occurs, so that only ethylene chloride can still yield the blue-violet. This example justifies the assumption of the existence of different unsoaped forms, which can determine the direction in which development occurs.

As with the sulphonamoyl derivatives, the great influence on the colour of the soaped dyeing which results from shifting the chlorine in the anthraquinone nucleus of VI from the 7- to the 6-position becomes explainable (Fig. 33). No matter in what

manner it is soaped, the latter dye always leads to the dichroic  $\beta_3$  form. Comparison with the corresponding stage of development of VI shows that only a slight difference in shade exists. Thus, the influence of chlorine in the 7-position is due mainly to the fact that it permits formation of the  $\beta_3$  form.

With 1-*p*-dimethylsulphamoylbenzamido-4-benzamidoanthraquinone (II) and similar dyes soaping at the boil always produces a brilliant red showing positive dichroism and a double maximum, viz.  $\beta_2$ . The similarity of the absorption spectrum to that of 1,4-diaminoanthraquinone is in fact amazing, and clearly shows that the resonance system must be very similar (Fig. 29). The spectrum has the inflection in the short-wave region, as well as the two maxima, which, however, are about equally strong, but the curve as a whole is displaced somewhat towards longer wavelengths. One difference, however, should be noted. In the case of the diamino compound the resonance system is stable in solution as well. The nature of the environment, i.e. the polarity of the solvent, and, in the case of dyeings, the kind of substrate, has an effect on the position of the mesomeric equilibrium, resulting in a change in colour within the red-violet to blue-violet region. The polarisation must be strongest in the crystalline state, for the crystals obtained from nitrobenzene or acetone show, if finely ground in water, an absorption spectrum in the blue-green with a weak double maximum. The crystals are anisotropic (II violet, I blue-green). With the *p*-dimethylsulphamoyl derivative (II), on the other hand, the  $\beta_2$  form is stable only in the adsorbed or in the crystalline state, but not in solution, and the position of the maxima does not depend on the environment.

The fact that 1,4-diaminoanthraquinone vapour shows only one maximum, at 492  $m\mu$ ,<sup>21</sup> suggests that, as in the case of Indigo vapour, which is red as well, the completely non-polar form is present, corresponding to the unsoaped form of the *p*-dimethylsulphamoyl derivative (II) with a maximum at 496  $m\mu$ . The stability of the non-polar form of 1,4-diaminoanthraquinone is so small, however, that it is not possible to isolate it\*.

If the unsoaped *p*-dimethylsulphamoyl derivative (II) is developed with polar solvents, an intermediate violet colour is sometimes obtained. With benzyl alcohol the development is arrested at this stage (Fig. 15). Obviously the colour-dichroic  $\beta_3$  form is present. With this form a further alternative is that the second amide group may either correspond to the state in  $\beta_1$ , as formulated above, or be completely rotated out of the plane and show no hydrogen bonds. The lack of resistance to alkali of the violet form of the *p*-dimethylsulphamoyl derivative (II) as well as of the violet modification, which results in combination with 1,4-dibenzamidoanthraquinone (I), together with the solubility in alcohol, make it likely that,

in contrast to the *p*-methoxy derivative (VIII), the second variant is present.

If the benzoyl group in the *p*-dimethylsulphamoyl derivative (II) is replaced by the cinnamoyl group, soaping again yields the  $\beta_2$  form (Fig. 34). The colour is only very slightly shifted to the yellow side. This agrees with the interpretation that this group, rotated out of the plane, does not take part in the mesomerism. In contrast to this, in the  $\beta_1$  state the cinnamoyl group exerts a very strong effect on the colour.

The bisdimethylsulphamoyl derivative (III) shows the effect of the substrate: on cotton the  $\alpha_1$  form is stabilised, so that, on soaping, the orange-brown negatively dichroic  $\beta_1$  form is produced. On viscose rayon or Cellophane, however, transition to  $\alpha_2$  can occur, so that on soaping conversion to the positively dichroic brilliant red of the  $\beta_2$  form becomes possible (Fig. 1 and 9).

So far it has not been possible to establish a definite relationship with fibre structure, and it is uncertain whether other factors, e.g. state of the vat and method of reoxidation, also play a part.

The remarkably great effects of various sulphamoyl groups on the colour of the soaped dyeing can be explained by assuming that development sometimes leads to the  $\beta_1$  form and sometimes to the  $\beta_2$  form: Whilst with the *p*-dimethylsulphamoyl derivative (II) the red  $\beta_2$  form is obtained, with the *p*-diethylsulphamoyl compound (IV) the orange negatively dichroic  $\beta_1$  form is produced (Fig. 35). The bis-substituted derivatives show exactly the opposite behaviour.

The same mechanism is responsible for X giving only a relatively weak orange. Soaping leads only to the negative dichroic  $\beta_1$  form, thus causing a great difference in shade as compared with II, whereas the *p*-chloro-homologous IX likewise leads to the  $\beta_2$  state. Hence practically no difference in shade is to be observed compared with II.

Summing up it can be said that, when considering the effect of a substituent, it is necessary to take into account, not only its direct effect, but also its effect on the nature of the resonance system formed, which is of far greater importance. Significant comparisons can therefore be made only among the three isomeric states  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ .

If, for example, the  $\beta_2$  state is selected, it is found that negative substituents have a bathochromic effect in the 6,7-positions of the anthraquinone nucleus, but a hypsochromic effect in the benzoyl groups, whereas positive substituents have the converse effect.

This corresponds exactly to Pfeiffer's substitution rule for quinydrones<sup>22</sup>, according to which positive auxochromes have a bathochromic effect if introduced into the cationic part, but a hypsochromic effect if introduced into the anionic part, whilst negative auxochromes behave conversely. This is an elegant confirmation of the postulated structure of the  $\beta_2$  form, which corresponds basically to an intramolecular quinydrone (Fig. 36). Different rules apply to the  $\beta_1$  and  $\beta_3$  states.

The three forms— $\beta_1$ ,  $\beta_2$  and  $\beta_3$ —are to be considered as hitherto unknown types of isomer.

\* Egerton and Roach<sup>23</sup> have recently reported that 1,4-diaminoanthraquinone in the solid state has only one maximum, at 550  $m\mu$ . We are not able to confirm this. But as these authors used quartz plates covered by sublimation in a high vacuum, it is possible that in this case the dye was deposited in an amorphous form; but it is equally possible that a different modification of the dye is formed. A number of simple anthraquinone disperse dyes are known to occur in different crystalline forms.



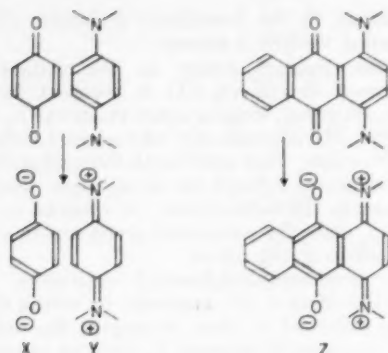


FIG. 36.—Comparison of the Formation of a Quinhydrone from an Anionic Part (X; e.g. *p*-Quinone) and a Cationic Part (Y; e.g. Tetramethyl-*p*-phenylenediamine) and the Transition from the  $\alpha_2$  form to the double ionic  $\beta_2$  Structure (Z)

The characteristic differences are of a steric nature based on differences in the planarity of molecules stabilised by hydrogen bonds. Since these bonds are very weak, the isomers can only exist under conditions where rotation of the molecules is hindered, i.e. in contact with a substrate or in solid form where the contact from molecule to molecule brings about stabilisation. As soon as they are in solution or in vapour form, the bonds are ruptured and the differences vanish. We therefore call these forms *contact isomers*. They show a certain relationship with those quinhydrone found by Weitz<sup>27</sup>, which also can exist only in adsorbed form, e.g. on aluminium oxide.

#### Dye Molecules in Crystalline Systems

With 1,4-dibenzamidoanthraquinone the dye is present in colloidal solution in the  $\beta_1$  state, as in the soaped dyeing. In the crystal, however, it is in a state which cannot be described by any of the formulae (Fig. 12). It is likely that there are dipole-dipole interactions or intermolecular hydrogen bonds between the individual molecules.

With the  $\beta$ -modification of the *p*-dimethylsulphamoyl derivative (II) the molecules are in the  $\beta_2$  form, but with the  $\alpha$ -form it cannot be decided whether they correspond to the  $\alpha_1$ ,  $\alpha_2$ , or  $\beta_1$  state.

For XI it must be admitted that the small difference between the  $\alpha_1$  and the  $\beta_1$  state is responsible for the existence of the orange-red and the bluish-violet crystals. Strong support is given to the proposed hypothesis by the fact that, in this case, in contrast to II, no change in the crystalline form is to be observed, despite the great difference in shade between the orange and the violet form. This is apparent from the X-ray diagrams. Therefore, the orange form can be changed into the violet form within the same crystal.

It has not been found possible to offer any explanation as to why certain substituents promote transition of the molecules into the  $\beta_1$  or the  $\beta_2$  state, or why certain substituents, and also certain developing agents, favour the  $\alpha_1$  or the  $\alpha_2$  form, which then gives rise to the  $\beta_1$  or the  $\beta_2$  state.

#### 19. CONCLUSIONS

A change in colour on developing a vat dyeing will always occur if the dye, after reoxidation, is first produced in a metastable form which is stabilised by adsorption on the substrate, so that a certain activation energy is required to attain the most stable state of the dye under these conditions. If the differences in stability are great enough, it may be possible to obtain these forms in colloidal solution or even as crystalline modifications.

The stability of these forms may be quite different in a different environment, e.g. in organic solvents. There are obvious parallels between these phenomena and the changes in colour which can be observed with organic-solvent solutions<sup>28</sup> and are termed *solvatochromism* and *thermochromism*. Like these phenomena, the changes due to soaping cannot be ascribed to one single cause, and the different possibilities of molecular variations such as isomerism, multimerism, and mesomerism must all be taken into account.

\* \* \*

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(MS. received 26th August 1959)

#### References

- Haller, R., *Melliand Textilber.*, **6**, 669 (1925); Bean, P., and Rowe, F. M., *J.S.D.C.*, **45**, 67 (1929).
- Valko, E. I., *J. Amer. Chem. Soc.*, **63**, 1433 (1941); Kornreich, E., *J.S.D.C.*, **58**, 177 (1942).
- Koch, J., *Helv. chim. Acta*, **24**, 187 E (1941).
- Wegmann, J., *Textil-Rund.*, **8**, 4, 97, 157 (1953).
- Waters, E., *J.S.D.C.*, **66**, 544 (1950); Sumner, H. H., Vickerstaff, T., and Waters, E., *ibid.*, **69**, 181 (1953); Sumner, H. H., *Hexagon Digest*, (16) 13 (1953).
- Müller, J., *Textil-Rund.*, **8**, 622 (1953); Wegmann, J., *ibid.*, **8**, 624 (1953); Sumner, H. H., and Vickerstaff, T., *J.S.D.C.*, **70**, 238, 413 (1954); Kornreich, E., *ibid.*, **69**, 297 (1953); **70**, 238, 413 (1954); Wegmann, J., *ibid.*, **70**, 412 (1954).
- Haller, R., *Kolloid Z.*, **29**, 95, 190 (1921); Haller, R., and Novak, A., *Kolloid Beih.*, **13**, 61 (1920); Auerbach, R., *Melliand Textilber.*, **8**, 160 (1927).
- Boulton, J., and Morton, T., *J.S.D.C.*, **56**, 143 (1940); **62**, 273 (1946).
- Joss, K., *S.V.F. Fachorgan*, **8**, 393, 444, 497, 548 (1953).
- Schaeffer, A., *Melliand Textilber.*, **38**, 428, 533 (1957).
- Scholl, R., *Ber. deutsch. chem. Ges.*, **44**, 1448 (1911).
- Egerton, G. S., and Gail, F., *Nature*, **181**, 1399 (1958).



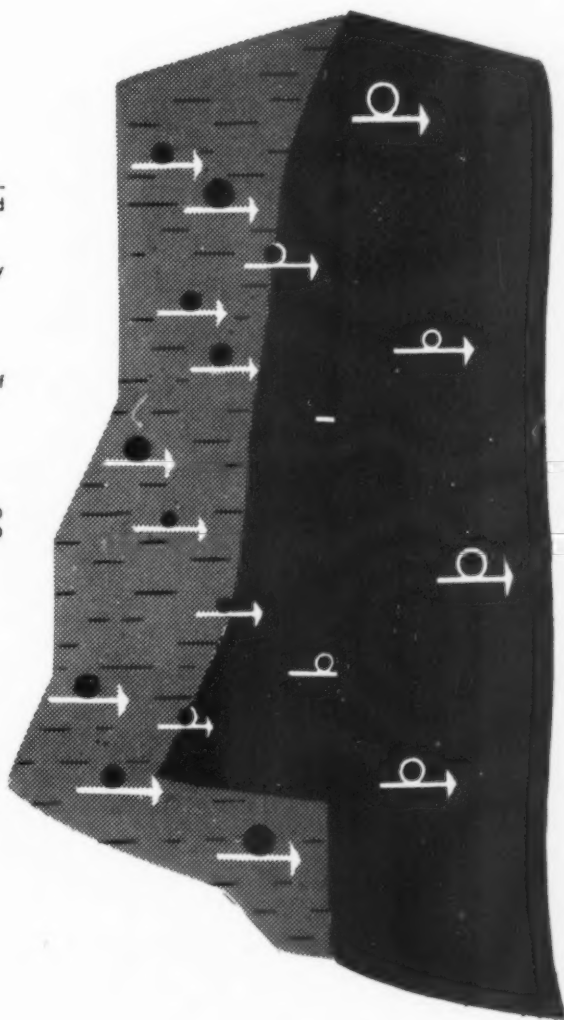
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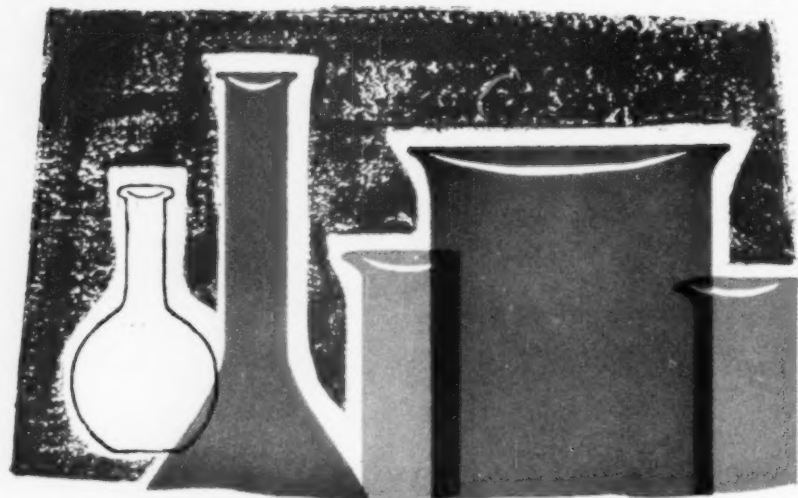
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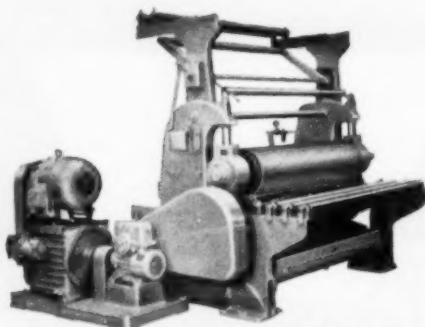
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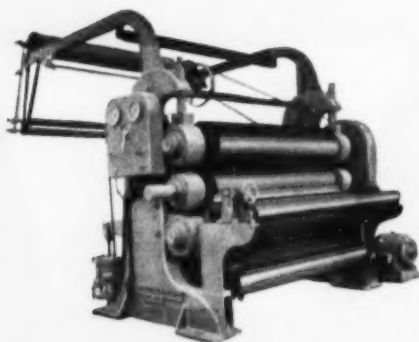
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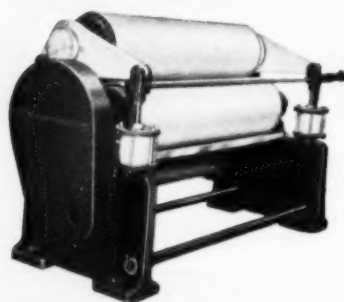
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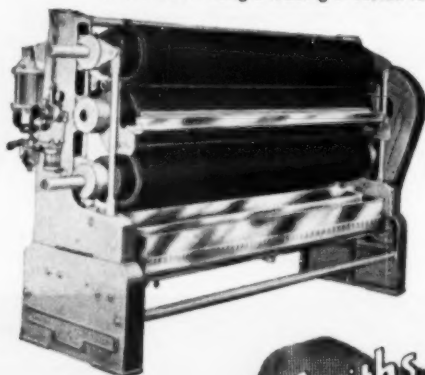


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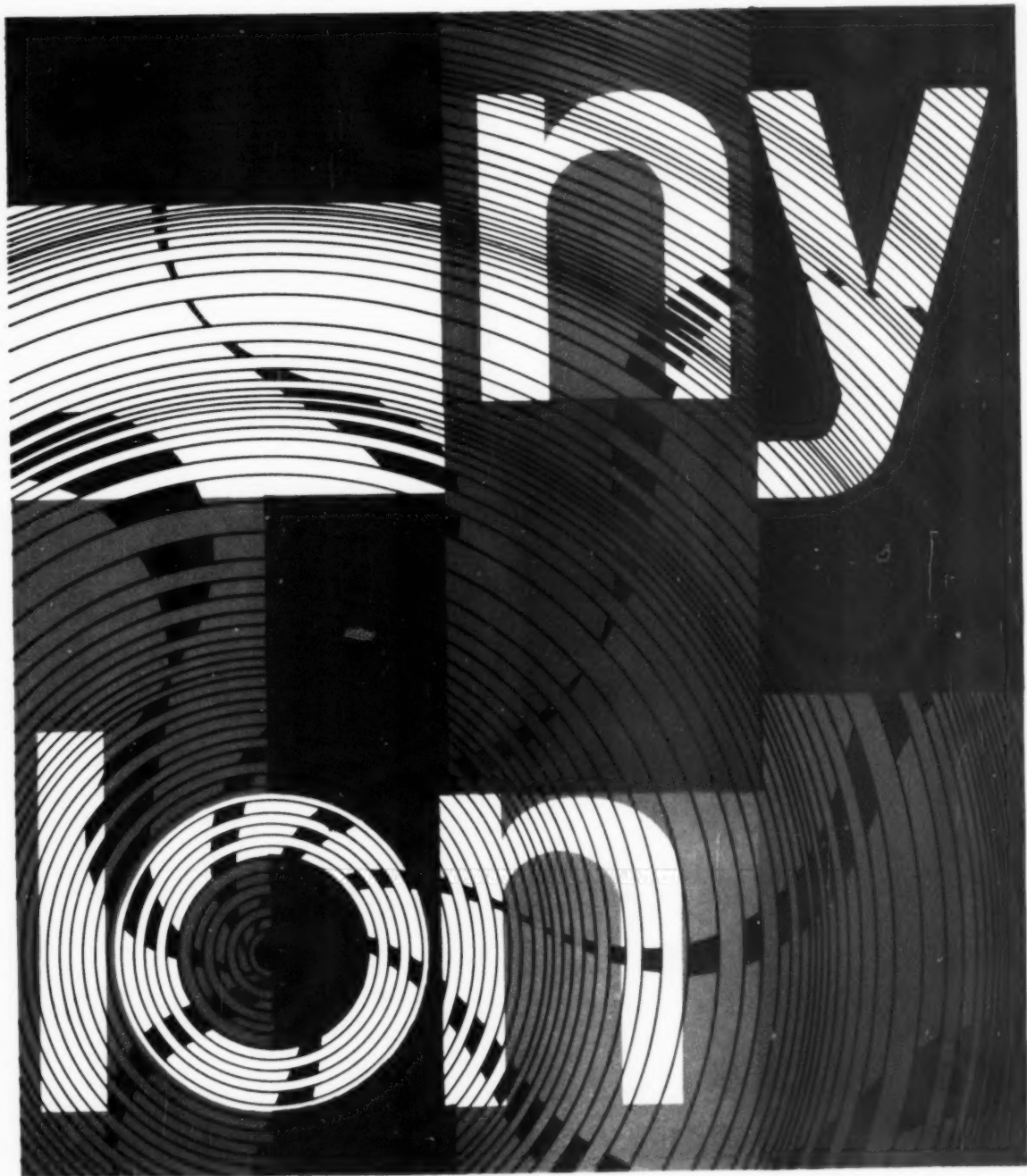
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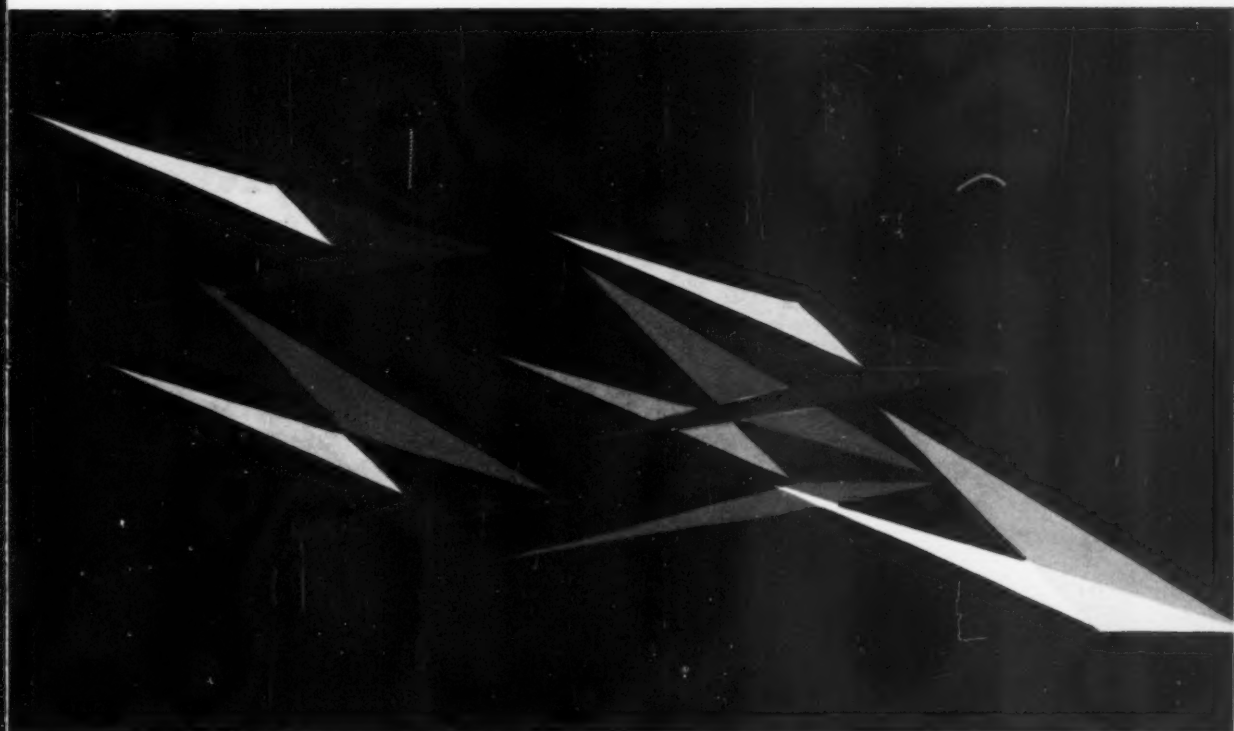
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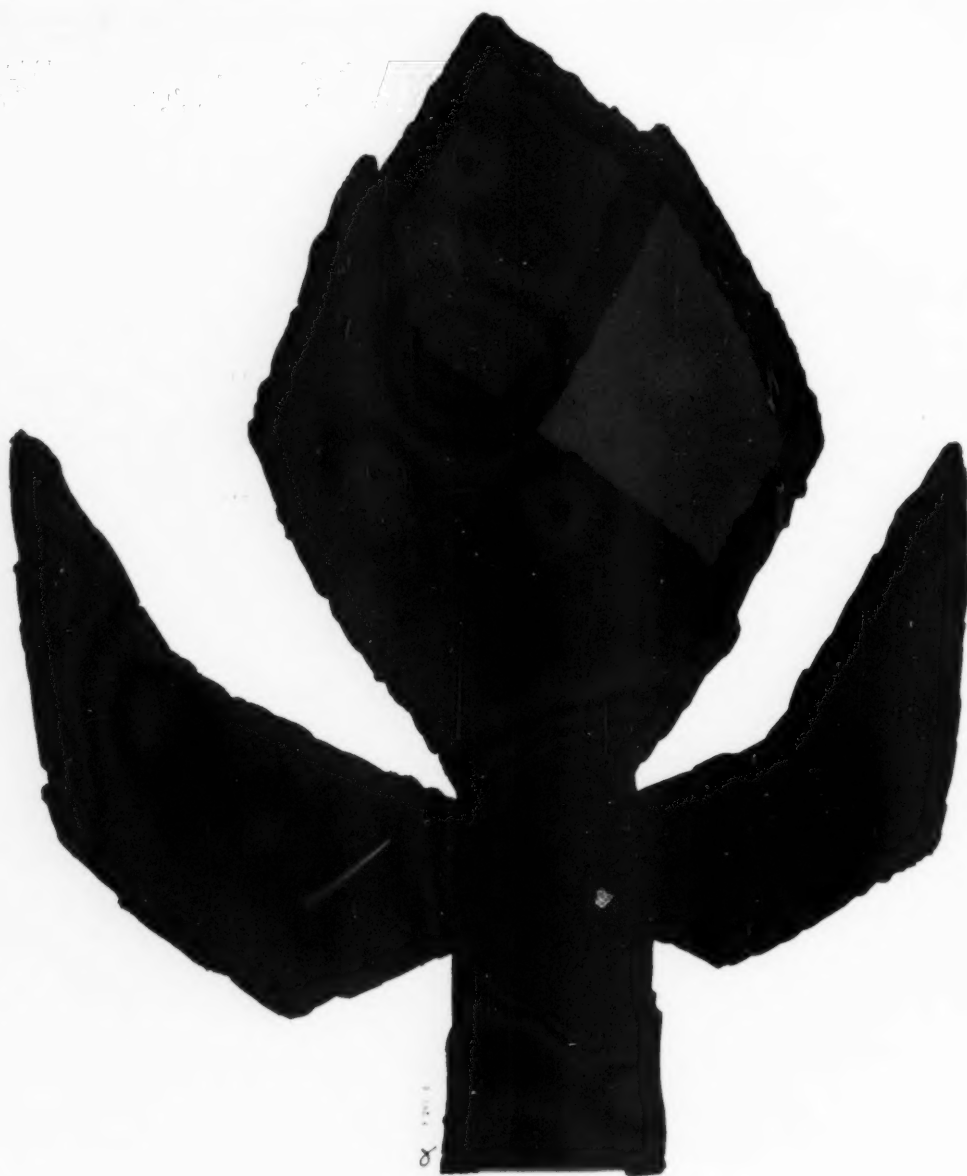
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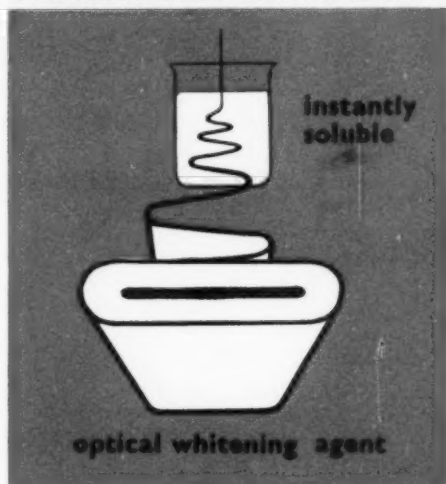


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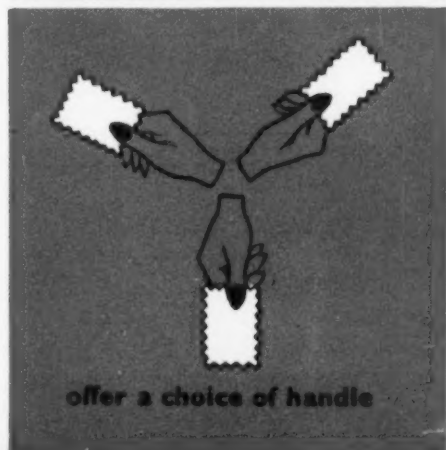
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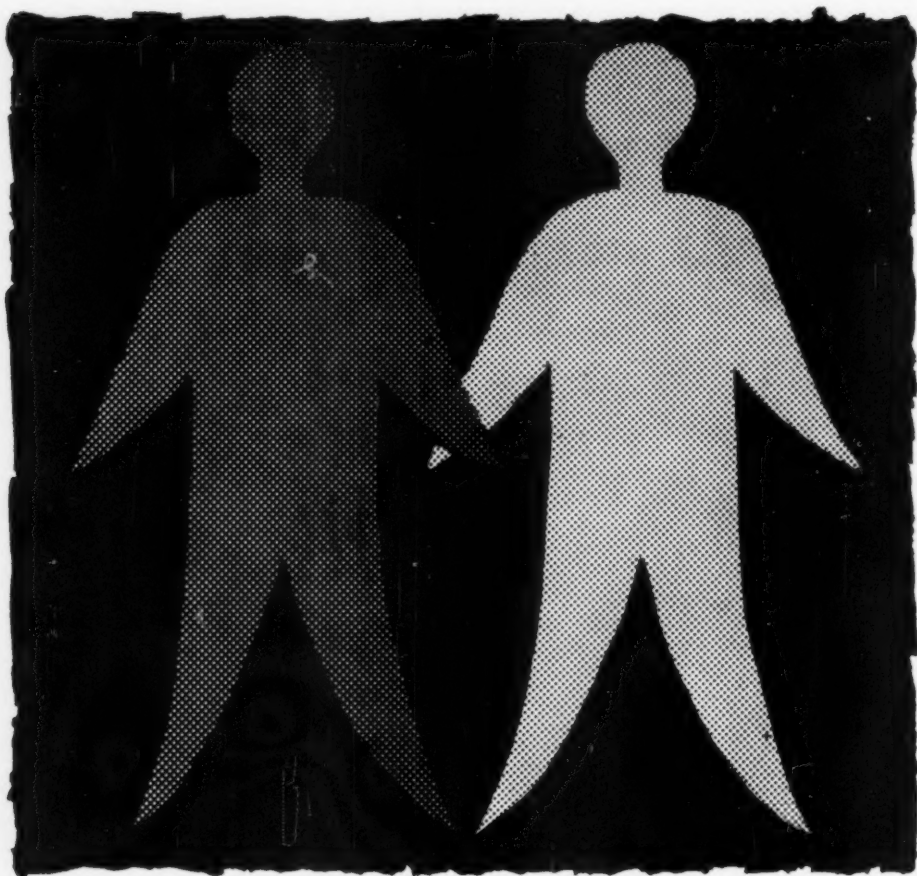
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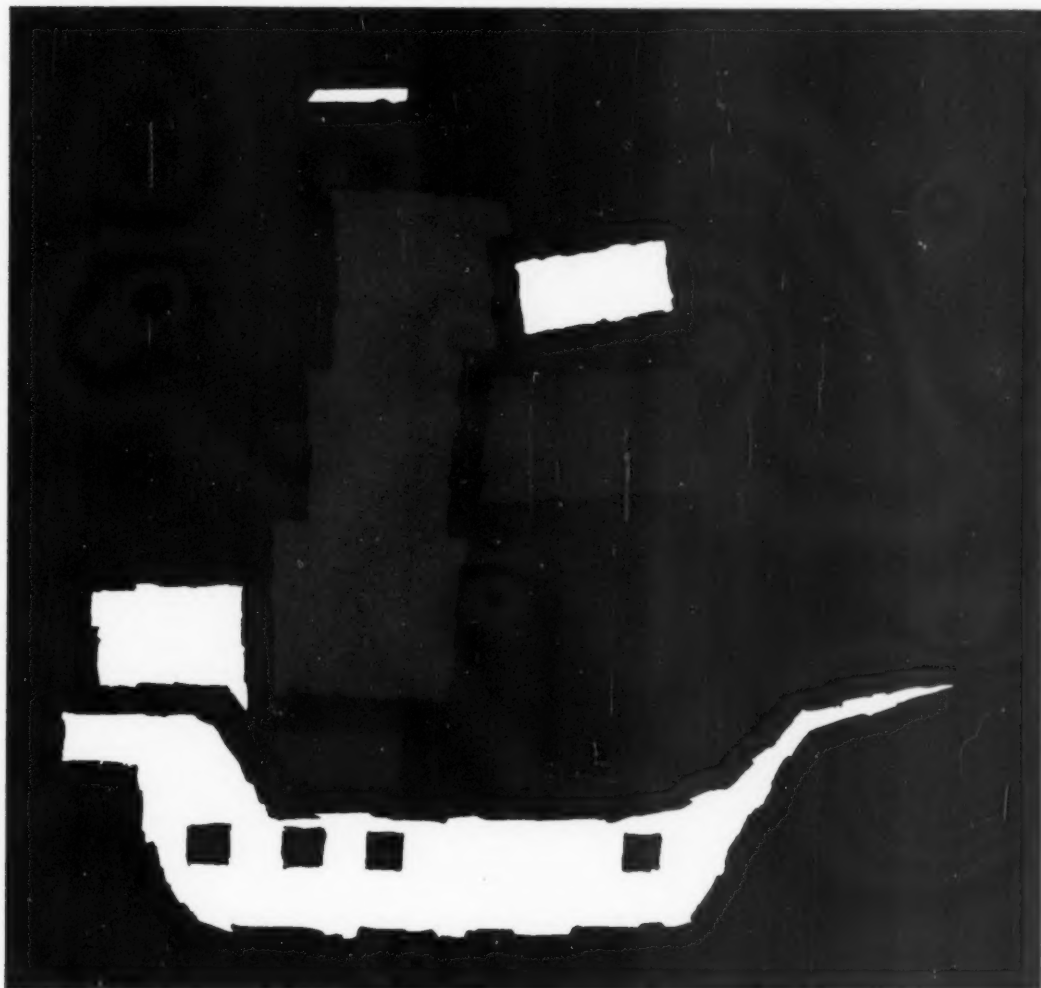
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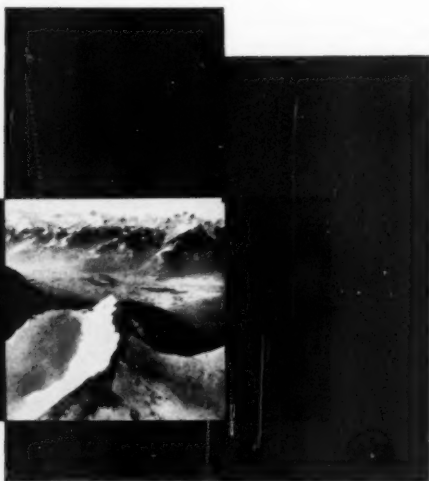




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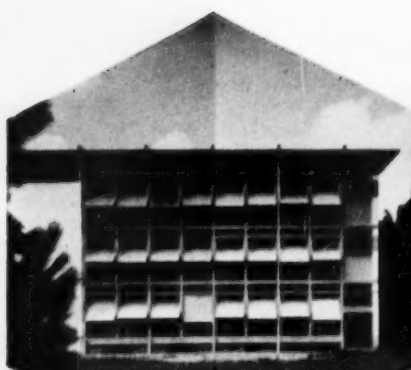
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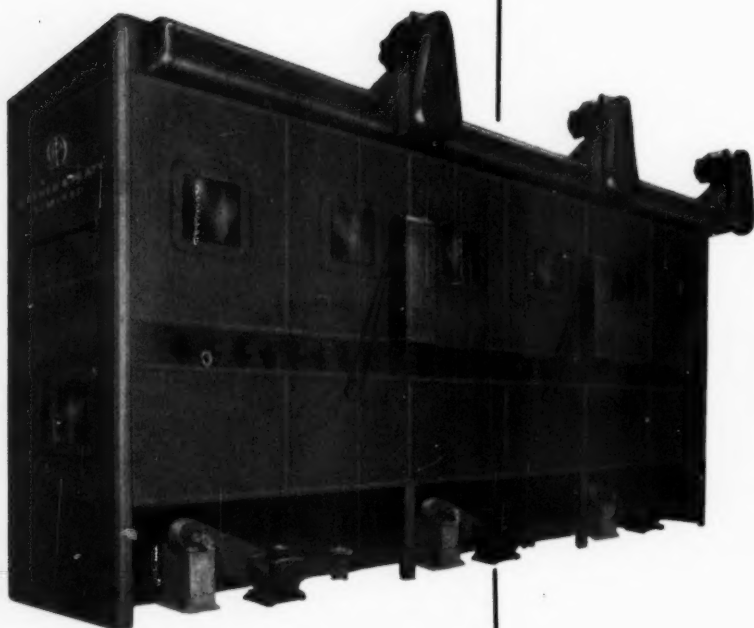
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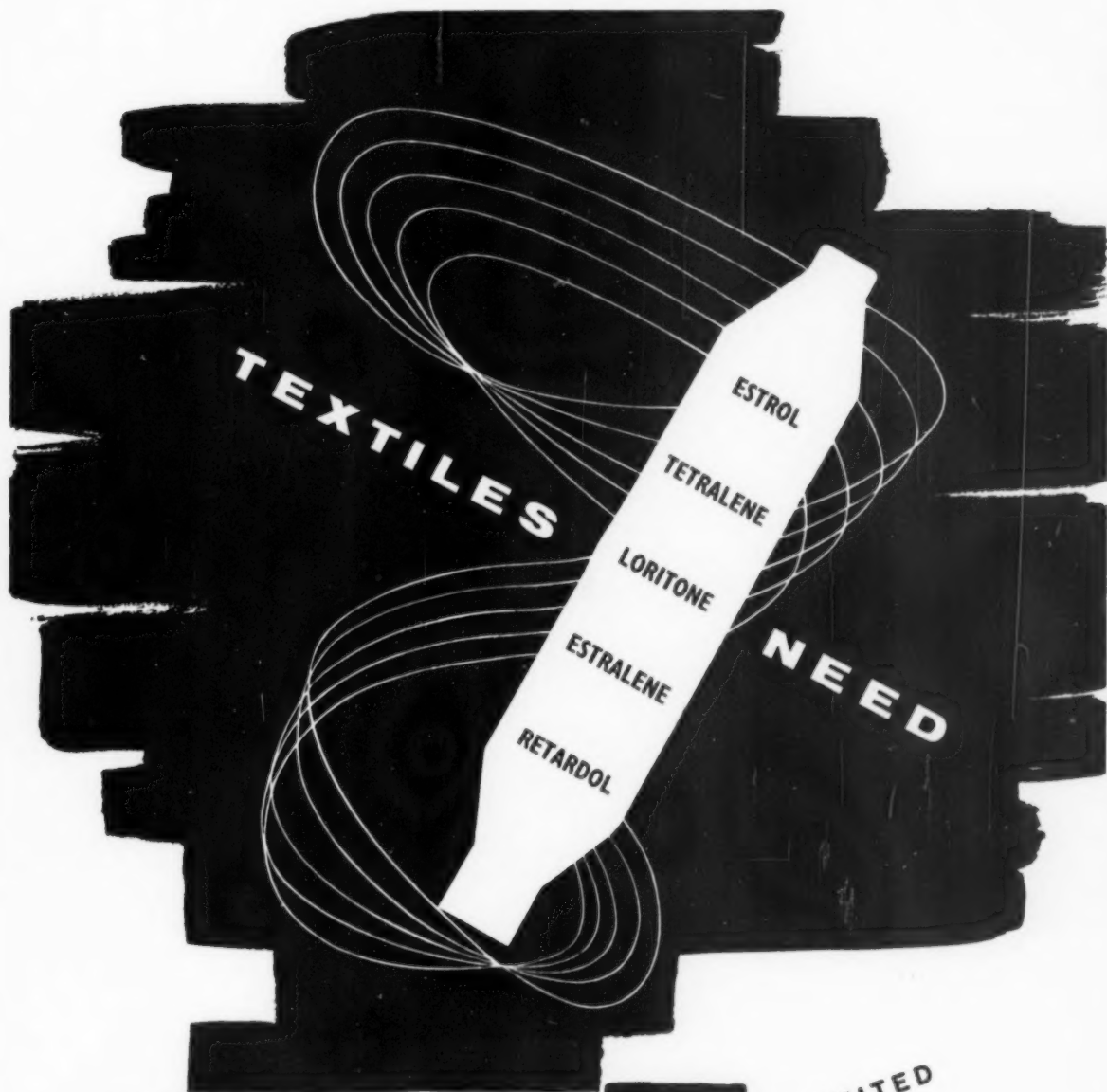
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- <sup>12</sup> Weitz, E., and Schmidt, F., *Ber. deutsch. chem. Ges.*, **72**, 2105 (1939).
- <sup>14</sup> von Susich, G., *P.B. Reports* 70,342, **1**, 14314–14350.
- <sup>15</sup> Stäuble, M., Unpublished work.
- <sup>16</sup> Bunn, C. W., *Chemical Crystallography* (Oxford 1945), pp. 5 and 6.
- <sup>17</sup> Pfeiffer, P., *J. pr. Chem.*, **109**, 191 (1924).
- <sup>18</sup> Richards, R. E., and Thompson, H. H., *J.C.S.*, 1260 (1947);  
Lüttke, W., and Mecke, R., *Z. Elektrochem.*, **53**, 241 (1949).
- <sup>19</sup> Allen, C. F. V., Wilson, C. V., and Frame, G. F., *J. Org. Chem.*, **7**, 169 (1942).
- <sup>20</sup> Peters, R. H., and Sumner, H. H., *J.C.S.*, 2101 (1953).
- <sup>21</sup> Flett, M. St. C., *ibid.*, 1441 (1948).
- <sup>22</sup> Sheppard, S. E., and Newsome, P. T., *J. Amer. Chem. Soc.*, **64**, 2937 (1942).
- <sup>23</sup> Merian, E., *Chimia*, **13**, 181 (1959).
- <sup>24</sup> Moran, J. J., and Stonehill, H. I., *J.C.S.*, 765 (1957).
- <sup>25</sup> Egerton, G. S., and Roach, A. G., *J.S.D.C.*, **74**, 401 (1958).
- <sup>26</sup> Pfeiffer, P., *Organische Molekülverbindungen* (Stuttgart 1927), p. 284.
- <sup>27</sup> Weitz, E., *Angew. Chem.*, **66**, 658 (1954).
- <sup>28</sup> Dimroth, K., *Marburger Sitzungsber.*, **76**, 3, 3–49 (1953);  
Schönberg, A., Mustafa, A., and Asker, W., *J. Amer. Chem. Soc.*, **76**, 4134 (1954);  
Kortüm, G., *Angew. Chem.*, **70**, 14 (1958).

### Discussion

Mr. E. KORNREICH: In 1942, when I put forward new ideas about the colour change of vat dyes on soaping<sup>2</sup>, the aggregation theory was the accepted explanation of the colour change. Dr. Wegmann's work is a most valuable contribution to our knowledge of dyes. I agree with him that little is yet known about these problems, but I feel that more is known than he admits. Dr. Wegmann has described an extensive series of experiments and has propounded one theory, whilst simultaneously equally extensive work has been described by Dr. Warwicker, who has put forward a different theory. This apparent difference of opinion may disappear if I remove a misconception from Dr. Wegmann's mind.

When, in 1942, I suggested on the basis of convincing experiments that crystallisation was the factor governing colour change, and when all the other British workers on this subject who confirmed my work speak of crystallisation, we do not mean that visible crystals (microscopic or otherwise) are being formed in the fibre. What we mean is that a rearrangement of the molecules of vat dyes occurs in the form of an orderly crystal lattice, causing a change in the vibration pattern of the molecules and thus a change of colour. On this basis, there is obviously little difference between the two conceptions.

Furthermore, all the evidence adduced by Dr. Wegmann fully confirms the crystallisation theory. Substitution of parts of the molecule by different groups will obviously change the relationship of these forces inside the molecule which are responsible for crystallisation, and thus lead to different colour changes. I suggest that, in fact, Dr. Wegmann's work has proved the crystallisation theory to be correct.

Dr. WEGMANN: Sumner, Vickerstaff, and Waters<sup>5</sup> commented as follows on Mr. Kornreich's work<sup>2</sup>—“Summarising present ideas upon the colour changes which occur in the soaping of vat dyes, Kornreich concludes that these are due to crystallisation, the necessary preliminary being dispersion.”

In fact, compared with the contributions made by Haller<sup>1</sup>, by Bean and Rowe<sup>1</sup>, and by others, he has not contributed any new momentum. These authors spoke of the formation of aggregates through agglomeration or crystallisation (e.g. the masking of the lustre of the fibre is due to the coagulation or crystallisation of the colouring matter into larger aggregates within the fibre). They left the question open—since they had not investigated it sufficiently closely—whether only amorphous or crystalline aggregates or both are formed. Kornreich's conclusion was that, in dyeings, a transition from (apparently amorphous) aggregates through a dispersion phase into crystalline aggregates takes place, but he did not provide any experimental proof. Therefore, a discussion of the soundness of his arguments is hardly possible. He recently claimed (*J.S.D.C.*, **69**, 297 (1953); **70**, 238 (1954)) that the crystals which are formed in the fibre are very small and invisible (microscopically and otherwise) and deduced from this that the difference between the two conceptions is slight. These alternatives, viz. large crystals—great difference, small crystals—slight difference, in my opinion miss the essence of the problem, since it is not a gradual but a fundamental difference that is involved.

Only unsaturated compounds are coloured, and their absorption bands move farther into the visible region the more extensive the conjugated system. The  $\pi$ -electron system of a molecule is not constant for a given chemical constitution, but is influenced to a greater or lesser extent by the state of the molecule, e.g. whether it is in the vapour form, the dissolved form, the adsorbed form, or the crystalline form. The  $\pi$ -electron system of molecules in the various forms can, in turn, be influenced by polarisation, dimerisation, multimerisation, association, tautomerism, alteration of the steric configuration, intramolecular hydrogen bonds, etc. These effects may occur either alone or in conjunction with one another and, according to the state of the molecule, in the same or different ways. If such differences are present in the vapour form or in various solvents, they can be maintained during the transition into the crystalline state, so that physically different, so-called *polymorphous* crystal forms result. When comparison is made between molecules of a substance in the dissolved, adsorbed and crystalline state, this possibility has to be borne in mind. A certain minimum number of molecules is required for the formation of a three-dimensional crystal. It is thus very important to realise that the molecules of a substance can have completely different properties—despite the same colour and, in consequence, the same influence on the  $\pi$ -electron system—depending on whether they are in a dissolved, adsorbed or crystalline form. In this connection it is of interest to note that, with dye III, the  $\alpha$ - and the  $\beta$ -crystal modification both possess poor light fastness (rating 4), when used for mass coloration, whereas the vat dyeing on the same substrate but containing adsorbed molecules shows a rating of 6–7 when unsoaped, and 7–8 when soaped, despite the fact that the colour of the soaped dyeing is



**AZONINE  
AND  
DURANTINE  
DYESTUFFS  
FOR  
COTTON**



*Town End Chemical Works Limited*

**BRAMLEY LEEDS**

- <sup>12</sup> Weitz, E., and Schmidt, F., *Ber. deutsch. chem. Ges.*, **72**, 2105 (1939).  
<sup>13</sup> von Susich, G., *PB Reports* 70,342, 1, 14314–14350.  
<sup>14</sup> Stauble, M., Unpublished work.  
<sup>15</sup> Bunn, C. W., *Chemical Crystallography* (Oxford 1945), pp. 5 and 6.  
<sup>16</sup> Pfeiffer, P., *J. pr. Chem.*, **109**, 191 (1924).  
<sup>17</sup> Richards, R. E., and Thompson, H. H., *J.C.S.*, 1260 (1947);  
 Lutke, W., and Mecke, R., *Z. Elektrochem.*, **53**, 241 (1949).  
<sup>18</sup> Allen, C. F. V., Wilson, C. V., and Frame, G. F., *J. Org. Chem.*, **7**, 169 (1942).  
<sup>19</sup> Peters, R. H., and Sumner, H. H., *J.C.S.*, 2101 (1953).  
<sup>20</sup> Flett, M. St. C., *ibid.*, 1441 (1948).  
<sup>21</sup> Sheppard, S. E., and Newsome, P. T., *J. Amer. Chem. Soc.*, **64**, 2937 (1942).  
<sup>22</sup> Merian, E., *Chimie*, **13**, 181 (1959).  
<sup>23</sup> Moran, J. J., and Stonehill, H. I., *J.C.S.*, 765 (1957).  
<sup>24</sup> Egerton, G. S., and Roach, A. G., *J.S.D.C.*, **74**, 401 (1958).  
<sup>25</sup> Pfeiffer, P., *Organische Molekülverbindungen* (Stuttgart 1927), p. 284.  
<sup>26</sup> Weitz, E., *Angew. Chem.*, **66**, 658 (1954).  
<sup>27</sup> Dimroth, K., *Marburger Sitzungsber.*, **76**, 3, 3–49 (1953);  
 Schönberg, A., Mustafa, A., and Asker, W., *J. Amer. Chem. Soc.*, **76**, 4134 (1954);  
 Kortüm, G., *Angew. Chem.*, **70**, 14 (1958).

### Discussion

Mr. E. KORNREICH: In 1942, when I put forward new ideas about the colour change of vat dyes on soaping<sup>2</sup>, the aggregation theory was the accepted explanation of the colour change. Dr. Wegmann's work is a most valuable contribution to our knowledge of dyes. I agree with him that little is yet known about these problems, but I feel that more is known than he admits. Dr. Wegmann has described an extensive series of experiments and has propounded one theory, whilst simultaneously equally extensive work has been described by Dr. Warwicker, who has put forward a different theory. This apparent difference of opinion may disappear if I remove a misconception from Dr. Wegmann's mind.

When, in 1942, I suggested on the basis of convincing experiments that crystallisation was the factor governing colour change, and when all the other British workers on this subject who confirmed my work speak of crystallisation, we do not mean that visible crystals (microscopic or otherwise) are being formed in the fibre. What we mean is that a rearrangement of the molecules of vat dyes occurs in the form of an orderly crystal lattice, causing a change in the vibration pattern of the molecules and thus a change of colour. On this basis, there is obviously little difference between the two conceptions.

Furthermore, all the evidence adduced by Dr. Wegmann fully confirms the crystallisation theory. Substitution of parts of the molecule by different groups will obviously change the relationship of these forces inside the molecule which are responsible for crystallisation, and thus lead to different colour changes. I suggest that, in fact, Dr. Wegmann's work has proved the crystallisation theory to be correct.

Dr. WEGMANN: Sumner, Vickerstaff, and Waters<sup>5</sup> commented as follows on Mr. Kornreich's work<sup>2</sup>—“Summarising present ideas upon the colour changes which occur in the soaping of vat dyes, Kornreich concludes that these are due to crystallisation, the necessary preliminary being dispersion.”

In fact, compared with the contributions made by Haller<sup>1</sup>, by Bean and Rowe<sup>1</sup>, and by others, he has not contributed any new momentum. These authors spoke of the formation of aggregates through agglomeration or crystallisation (e.g. the masking of the lustre of the fibre is due to the coagulation or crystallisation of the colouring matter into larger aggregates within the fibre). They left the question open—since they had not investigated it sufficiently closely—whether only amorphous or crystalline aggregates or both are formed. Kornreich's conclusion was that, in dyeings, a transition from (apparently amorphous) aggregates through a dispersion phase into crystalline aggregates takes place, but he did not provide any experimental proof. Therefore, a discussion of the soundness of his arguments is hardly possible. He recently claimed (*J.S.D.C.*, **69**, 297 (1953); **70**, 238 (1954)) that the crystals which are formed in the fibre are very small and invisible (microscopically and otherwise) and deduced from this that the difference between the two conceptions is slight. These alternatives, viz. large crystals—great difference, small crystals—slight difference, in my opinion miss the essence of the problem, since it is not a gradual but a fundamental difference that is involved.

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identical with that of the  $\beta$ -modification. A chemical compound can occur in two forms with completely different  $\pi$ -electron systems, but identical crystal lattices. Dye XI serves as an example: its orange and violet forms possess the same crystal lattice and, consequently, can be converted into one another, even within the same crystal. So far as is known, this phenomenon has never hitherto been described, and no terms exist as yet to designate such forms. In this case, too, the two types of molecule in the crystal possess other properties than when in the adsorbed state.

My manuscript had already been prepared when Dr. Warwicker's papers were published (*J. Textile Inst.*, **50**, T 404, 443 (1959)). In this connection, I have never disputed the fact that, in a vat dyeing in the reduced, oxidised or soaped state, crystals can be present—both in and on the fibre—and that, under the influence of steam or as a result of soaping, crystal formation can occur. Most practical dyers are familiar with bronziness. In normal dyeings this does not take place, or only to an insignificant extent, and crystal formation is in no way related to the colour changes which occur during soaping. The procedure employed by Dr. Warwicker (100% or more dye, longer dyeing times at room temperature, etc.) no doubt promotes crystal formation. Dyeings of this type are not very suitable for determining the effects involved, since they are heterogeneous. However, it should be possible to produce homogeneous test material and to differentiate, not only between dye crystals and molecules, but also between adsorbed and unadsorbed molecules within the fibre. I hope to revert to this question at some later date, and to discuss it in conjunction with the problem of the dye-fibre linkage.

My position may be summarised as follows. Establishment of the molecular theory is not an end in itself: the aim is to build up a sound basis on which to study the problem of constitution and colour in relation to the substrate. The relationship between colour and constitution in dyes has hitherto been studied mainly by means of solutions, and in part also on crystals. However, it is well known that the substrate can have a great influence on the colour of a dye, and any future theory should cover not only chemical constitution, but also the influence of the substrate, as equal partners in relation to the colour of a dyeing.

Dr. G. BERTOLINA: When a polyester-cotton mixture is dyed with vat dyes, using the Thermosol process for the polyester fibre and the usual method for the cotton, the colours of the two fibres are sometimes the same and sometimes

different. Can the lecturer explain this fact on the basis of his theory?

Dr. WEGMANN: There is a connection between this phenomenon and the change in shade resulting from soaping. The shade of the Terylene dyeing usually corresponds to the colour of the dye in organic solvents, and greater deviations from the shade on the cotton are especially noticeable in the case of easily polarisable dyes with an extensive  $\pi$ -electron system, e.g. derivatives of pyranthrone and dibenzanthrone. The existence of various contact-isomeric forms (mentioned in the lecture) can also cause considerable differences between the cotton and Terylene dyeings, because all these forms are eliminated by dissolution of the dye in organic solvents.

Mr. A. S. FERN: Has the author studied the comparative behaviour of unmercerised cotton and mercerised cotton, insofar as the substrate affects the change of shade of a vat dye on soaping?

Dr. WEGMANN: As far as the effect of the substrate on the change of shade caused by soaping is concerned, it is necessary to differentiate between two types of dye. The first type, e.g. dibenzanthrone, shows the same behaviour on the substrate as it does in various solvents. Smooth transitions are observed which, in addition, are greatly dependent on the moisture content of the fibre. These dyes also show solvatochromism and thermochromism in organic solvents. The second type, represented by dye III, does not show solvatochromism and can change into two well-defined forms. The orange-brown, negative dichroic form is obtained on natural cellulose, and the brilliant red, positive dichroic form on regenerated-cellulose fibres. No connection with the structure of the substrate has yet been found, and it is not known to what extent other factors such as state of vat and type of oxidation are involved. In both cases no significant differences in "development" have been found which can be ascribed to mercerising.

Prof. E. ELÖD (*communicated*): The colour of a vat dye might be changed by the formation of a complex with the detergent during soaping.

Dr. WEGMANN: The formation of adsorption compounds between colloiddally dispersed vat dyes and polyethylene oxide condensation products in aqueous solution has been observed. Dye molecules adsorbed on cellulose are not affected, even when they are dispersed in a colloidal form by wet milling of the dyeing. Changes in shade occur under the influence of damp heat, and dispersing agents do not cause any alteration in "development".

## ERRATUM

On p. 136 of the February 1960 issue the number of the second patent abstract under Blends of Styrene Polymers and Rubbery Diene Polymers Coloured with Azo Dyes should read **USP 2,893,976** not USP 2,893,975.

## Notes

## Election of Fellows

At the meeting of Council held on 6th April 1960 the following elections were made—

Douglas Frederick Anstead

*Romford, Essex; Managing Director, D. F. Anstead Ltd., Romford, Essex*

Noel Bradbury

*Matley, Stalybridge, Cheshire; Manager, Textile Printing Department, John Walton of Glossop Ltd., Hollingworth, near Manchester*

Will Furness

*Dunstable, Bedfordshire; Senior Lecturer in Dyeing and Finishing, Leicester College of Technology and Commerce*

William Russell

*Kingsville, Victoria, Australia; Chemist, Wangaratta Woollen Mills Ltd., Wangaratta, Victoria, Australia*

## Death of Members

We regret to report the death of Miss E. Behrens, Mr. H. Birchall, and Mr. A. E. Waywell.

## The End of the Dyestuffs Acts

The Dyestuffs Acts in abeyance since 1939 though still in the statute book have now been repealed. Their passing marks the confidence of the British colour makers that they can withstand all competition and restores to the colour users that liberty of choice which they had voluntarily forgone for nearly two generations in the interests of the nation as a whole.

Mr. Erroll, Minister of State, Board of Trade, in moving the second reading of the European Free Trade Association Bill in the House of Commons on 15th February 1960, said that as a result of the E.F.T.A. obligation to eliminate quantitative restrictions on imports it had become necessary to replace the system, established under the Dyestuffs Acts, of prohibiting imports of intermediates, dyes and pigments except by licence, by a protective licence otherwise the British market would become wide open to duty-free imports from the E.F.T.A. Thus it was necessary to repeal the Dyestuffs Acts and replace them by a tariff on imported intermediates, dyes and pigments which will apply to those from all countries for 10 years, but after that imports from members of E.F.T.A. will be duty free.

This legislation came into effect on 2nd March 1960 and has had the effect that since then intermediates, dyes and pigments have been treated for other purposes exactly the same as other chemicals.

## Society of Chemical Industry

## Jubilee Memorial Lectures 1960-61

The two Jubilee Memorial Lectures to be given during the 1960-61 session are *Polymer Science in the University* by Prof. G. Gee and *The British Chemical Industry—from "K.I.D." to "Outer Seven"* by Mr. G. Brearley.

## Institute of Metal Finishing

## Annual Conference 1960

The annual Metal Finishing Conference will be held in Scarborough on 26-30th April 1960 and some of the papers to be read and discussed will be of interest to some tinctorial technologists. These papers include two on the sealing of anodic oxide films on aluminium and several on the use of lacquers, paints and resin finishes. Full particulars will be supplied on request by the Conference Secretary, Institute of Metal Finishing, 32 Great Ormond Street, London, W.C.1.

## Institute of Sewage Purification

## Annual Conference 1960

This conference will be held at Scarborough from 21-24th June 1960. A paper on *Development and Experiment in the Use of Biochemically Soft Detergents* to be introduced by Dr. A. Kay, Chief Chemical Inspector, Ministry of Housing and Local Government, will deal with work on production of detergents which will be broken down at the sewage works and so reduce foaming of rivers.



### The Second International Synthetic Rubber Symposium and Rubber Exhibition

This symposium and exhibition will be held in Church House, London S.W.1 on 11-13th October 1960. Further information regarding it can be obtained from the organisers—Rubber and Plastics Age, Gaywood House, Great Peter Street, London, S.W.1.

### 1960 Gordon Research Conference on Textiles

This conference will be held from 11-15th July 1960 in the Colby Junior College, New London, New Hampshire, U.S.A., under the chairmanship of Mr. Fred Fortess. The 9 papers to be read deal with the fundamental properties of cotton, nylon, polyester and acrylic fibres, the modification of cellulosic fibres, the mechanism of the dyeing of

polyamide fibres, and wash-and-wear finishes. Full information can be obtained from W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, R.I., U.S.A.

### Meetings of Council and Committees April

Colour Index Editorial Board—4th

Council—6th

Finance and General Purposes—6th

Publications—12th

Fastness Tests Co-ordinating—12th

Annual General Meeting—29th

Annual Meeting of Chairmen and Honorary Secretaries of Sections—29th.

## New Books and Publications

### Patents and Trade Marks in U.S.S.R.

Soviet Patent and Trade Mark Law. Report of a United Kingdom Delegation to the Soviet Union. Pp. 33. H.M. Stationery Office. Price, 2s. 6d.

Any manufacturer who has trade or expects to have trade with the U.S.S.R. will find it useful to study the Report, just published, of a visit to Moscow by a British Delegation in December 1959. This Report shows that very few patents in U.S.S.R. are sought by foreigners but concludes that as a rule "there is no legal way to stop the copying in the Soviet Union of U.K. inventions unless patents are obtained there". Fees, particularly renewal fees, are high but, as the Report says, "the U.K. owner of a worthwhile invention who proposes to sell goods embodying that invention to the U.S.S.R. has only the fees to lose and may . . . have a good deal to gain from seeking patents in the U.S.S.R."

The Report explains the procedure regarding protection for inventions in U.S.S.R. in a very clear manner and includes a short discussion on Trade Marks.

An interesting fact brought to light is that before Soviet goods are sold abroad they must bear a registered trade mark. Since the registration is not permitted of marks confusingly similar to those already on the register, "the registration of U.K. marks in the Soviet Union ought to ensure that competing Soviet exports to the third country in question do not bear similar marks".

Perhaps it is true to say, therefore, that any British manufacturer who expects to have to compete in any overseas country with U.S.S.R. manufacturers should study this Report, which concludes with a translation of the Law of 1959 concerning inventions, of the Trade Marks Law of 1936, and of a most useful explanatory pamphlet issued by the Patent Bureau of the U.S.S.R. Chamber of Commerce.

L. E. JONES

### Rezeptbuch für Faserstoff-Laboratorien

By P.-A. Koch. Pp. viii + 239. Berlin: Springer-Verlag. 1960. Price, DM.31.50.

This handbook describes a series of systems of qualitative and quantitative analysis applicable to all types of textile fibres. The tests include chemical and physical examination for the identification of fibres and finishing treatments, the quantitative analysis of fibres in mixtures, and of mordants, rapid spot tests for identification of the class of dye on dyed fibres, and detection of damage in fibres. Complete lists of required reagents are included.

The subject matter is attractively presented, the lay-out being carefully planned, and the volume is of convenient size and good appearance.

This work deserves a place in every textile laboratory.

C. H. GILES

## Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

### Badische Anilin- und Soda-Fabrik A.G.

CELLITON FAST ORANGE GF2R: CELLITON FAST SCARLET GF2R—These two disperse dyes give bright oranges and yellowish scarlets, respectively, on secondary cellulose acetate, the dyeings having good fastness to light, wet treatments, perspiration and particularly to burnt gas fumes. Dyeings of both are dischargeable to

white. Both dyes also have good affinity for cellulose triacetate. Fastness figures include—

	Light (Daylight)	Burnt Gas Fumes	Washing a
Fast Orange GF2R	6	4-5	4-5
Fast Scarlet GF2R	6-7	4-5	4-5



**CELLITON GREY GFB**—This disperse dye gives greys somewhat bluer in hue on secondary cellulose acetate rayon. Dyeings have good fastness to burnt gas fumes and show only slight reddening in artificial light. Celliton Fast Yellow 5R and Celliton Fast Scarlet R, which give dyeings having similar high fastness to burnt gas fumes, should be used for shading. Fastness figures include—Light (daylight) 4, burnt gas fumes 4-5, washing b 3, sublimation 4-5.

**INDANTHREN BROWNS LMG**—This homogeneous vat dye gives browns of very good all-round fastness on cellulosic materials and is recommended for dyeing materials required to withstand piece-bleaching and repeated laundering. It has good levelling properties and covers immature cotton well and is thus very suitable for use together with Indanthren Olive MW for olives and khakis. It also gives solid dyeings on mixtures of cotton and viscose. Fastness figures on cotton include—Light 7, washing (95°C.) 5, soda boiling 4-5, chlorine 5.

**FIXAPIRET 140**—A resin-finishing preparation for shrink-resist, minimum-iron and other types of finishes on cellulosic materials.

**GLYEZIN A**—A dye solvent for use in printing Vialon Fast, Neopalatin, Orlolan and Basacryl dyes.

**NEKANIL LN**—An alkyl aryl polyglycol ether for use as a non-ionic detergent for wool.

**PERSTABILISER BASF LIQUID AND POWDER**—A stabiliser for caustic alkaline bleach baths containing active oxygen.

**SILICOEN A15; A25; AF**—Solutions of colloidal silica for non-slip finishing of textiles. They have a slight delustering effect and also impart resistance to soiling.

**UNIFEROL W**—This is now recommended as the standard levelling agent for use when dyeing metal-complex, chrome and acid dyes on wool and wool/cellulosic fibre mixtures and also disperse, metal-complex and acid dyes on polyamides, polyesters, polyacrylonitriles and secondary cellulose acetate and triacetate. Similarly it is of use when dyeing jute, sisal and similar fibres with acid, basic and metal-complex dyes. It is also of interest for levelling uneven dyeings and partly stripping dyeings of metal-complex dyes.

#### Ciba Ltd.

**COMBATEX A**—A cationic synthetic resin emulsion free from plasticiser and recommended for imparting a firm handle to cellulosic, wool, and synthetic fibre materials and improving their resistance to abrasion.

**COMBATEX V**—A cationic synthetic resin emulsion free from plasticiser and recommended for imparting a full to crisp handle, fast to water and washing, on all types of materials.

#### J. R. Gelgy S.A.

**CUPHOPHENYL RED GL (No. 1309)**—This direct dye gives yellowish reds on cellulosic fibres when aftertreated on the fibre with copper sulphate. In combination with Rubine RL or Black BWL it gives deep bluish reds and bordeaux. It is also of interest for dyeing the cellulosic portion of wool/cellulosic fibre mixtures and direct printing. Fastness figures for an aftercoppered dyeing on spun viscose rayon include—Light 6-7, washing (Test b, 60°C.) 3-4, perspiration 4.

**IRGALAN AND IRGANOL 8 DYES ON KNITTING YARN**—This card contains dyeings in three depths on wool yarn of forty combinations of Irgalan and Irganol 8 dyes, recommended for complete compatibility of dyeing behaviour and giving dyeings of very good all-round fastness.

#### Imperial Chemical Industries Ltd.

**COOMASSIE TURQUOISE BLUE 3G**—This acid dye gives bright greenish blues on wool, similar in hue to those obtained with Disulphine Blue AN but of much better fastness to light and wet treatments. It is claimed that this new dye is outstanding in this respect and unapproached by other dyes of similar hue. Applied conventionally skittery dyeings are obtained and the recommended method is to set the dyebath with 3% of ammonium acetate and 1% of acetic acid (30%), circulate for 5-10 min. at 40-50°C. to equalise the pH, add 2% of Lubrol W, the required amount of dye, and 1% of Lissolamine A 50% Paste, circulating after each addition, if necessary. The temperature is raised to 95°C. during

30 min. and dyeing continued at 95°C. for 45-60 min. Yarns in cheese form may be dyed satisfactorily in circulating-liquor machines; for hank dyeing the two-attack type of Hussong machine is preferred. It is not considered generally suitable for dyeing cloth but may be used on unchlorinated knitted material. In certain machines addition of Silicone Antifoam M435 is advantageous. Very bright greens of good fastness may be obtained using Coomassie Turquoise Blue 3G and Procion Brilliant Yellow H5G by the recommended method. Fastness figures include—Light (Wilmalaw) 5-6 greener, alkaline milling 3-4, washing (S.D.C. No. 2, 45 min. at 50°C.) 4 redder.

**PROCIEN RUBINE HB**—This reactive dye gives full bluish reds of very good fastness to light and wet treatments when printed on cellulosic fibres. It has good solubility, builds up well and gives print pastes of good stability. The dry heat fixation method is suitable for all depths of prints if 20% of urea is added to the print paste. Fastness figures on cotton include—Light (Xenon arc) 6, washing (Test No. 5, 5 times at 100°C.) 4-5.

**PROCIEN BRILLIANT RED 8B**—When dyed on cellulosic fibres, this homogeneous reaction dye gives bright bluish reds, much bluer than those obtained with Brilliant Red 5B and much faster to hypochlorite bleaching, being comparable in this respect with Yellow R and Rubine B. It has high affinity for cellulose and is thus of particular interest for deep colours but for the same reason complete removal of unfixed colour may be difficult and after-treatment with Fixanol PN may be desirable. It resembles Brilliant Red 2B in that a little of the combined dye may be hydrolysed during storage under humid, acidic conditions and stain adjacent materials. The effect is insignificant on viscose rayon and not found at all with resin-finished materials. Fastness figures on cotton include—Light (Wilmalaw) 4, repeated severe washing (Test No. 5, 5 times at 100°C.) 3-4, hypochlorite bleaching 4 weaker, redder.

**PROCIEN BRILLIANT RED 8B**—When printed on cellulosic materials this reactive dye gives bright bluish reds of good fastness to light and wet treatments. Prints may be fixed using both steaming and non-steaming procedures. Fastness figures on cotton include—Light (Wilmalaw) 3-4, washing (Test No. 5, 5 times at 100°C.) 4-5.

**SUPRA LEMON CHROME 4G**—A greenish-yellow lead chrome pigment, recommended for full-depth paints of excellent weathering fastness, particularly high quality stoving enamels, and also for roller coating enamels, tin printing inks and in printing inks of all types.

**CIRRASOL HA**—A feebly cationic product for use as a fibre lubricant with all types of man-made fibres and also as a softening agent.

**FLUOLITE RP**—A fluorescent brightening agent possessing affinity for cellulose and particularly recommended for whitening paper. It gives a reddish fluorescence of only moderate resistance to light but of good stability to bleach, alkali and acids.

**RESIST SALT L**—A mild oxidising agent active under alkaline conditions. It is recommended for minimising faults in reduction discharge printing, in certain pad-development methods for applying reactive dyes, in kier boiling and mercerising.

**TECHNICAL INFORMATION LEAFLETS**—Dyehouse No. 527. *Procion Brilliant Blue H7G: Application to Cotton in Jig or Package-dyeing Machines*—A modified procedure is recommended for applying Procion Brilliant Blue H7G in short liquors whereby fixation is improved and the risk of specky dyeing is avoided. By carrying out the exhaustion stage and the initial fixation at a lower temperature (50-60°C.) the aggregation of the dye may be satisfactorily controlled and larger amounts of salt safely added.

Dyehouse No. 528. *Fastness to the Si-Ro-Set Method of Durable Pleating: Azoic, Direct, Procion, Sulphur, and Vat Dyes*—Since the Si-Ro-Set process for the durable pleating of wool cloths is likely also to be applied to wool/cellulosic fibre mixtures, the effect of this process on dyes applied to cellulosic fibres has been determined with respect to cotton.

Dyehouse No. 529. *Procion Dyestuffs: A Method for Reducing the Tendency of Dyed Materials to "Bleed" on Storage*—Addition of certain amines to the soaping-off

bath markedly reduces "bleeding" of dyeings produced by all methods except continuous methods with fixation in steam. The recommended procedure is to treat for 10-20 min. at the boil in a solution containing 1 part each of ethylene diamine and Lissapol ND. The treatment is not considered necessary with dyeings on viscose or any resin-treated materials.

**Dyehouse No. 530. Lissapol N in the Laundry—**Recommended washing formulae are given for washing woollens and coloured cottons and "silks", for which Lissapol N is very suitable since it is a very efficient detergent at relatively low temperatures. Since it is an excellent emulsifying agent, Lissapol N is also very good for washing engineers' overalls.

**Dyehouse No. 531. Wool Dyes: Fastness to the Immaculate Finish for Durable Pleading—**Figures are given for the fastness of the full range of dyeings on wool when treated according to three methods simulating commercial practice using the recently introduced process based on sodium bisulphite as the setting agent.

**Dyehouse No. 532. (Replaces No. 496). Weathering Fastness—Azotic Dyes—**Further specimens of the azo-dyed cloth have been exposed at Wilmalov between April and October 1959. These figures are presented together with those previously obtained. The 1958 figures were obtained during one of the wettest summers and those for 1959 during one of the driest and sunniest summers in this country on record and it is surprising that there are no significant differences between them.

**Dyehouse No. 533 (Replaces No. 473). Light Fastness of Dyes: I.S.O. and A.A.T.C.C. Ratings.**

**Dyehouse No. 534. Fixanol PN: Use with Copper Salts for Aftertreating Direct Dyes—**The combined use of the cationic dye-fixing agent, Fixanol PN, and copper salts minimises, and in certain cases prevents, the reduction in light fastness resulting from the use of the cationic agent alone. The general recommendation is that dyeings should be treated in a solution containing 0.5-2.0% of Fixanol PN and 0.2-0.8% of copper sulphate, treatment being commenced cold and the temperature gradually raised to 60-70°C. during 20 min. Fastness data for water, washing, and light are given for untreated, Fixanol PN treated, and Fixanol PN and copper sulphate treated dyeings of a selected range of direct dyes.

**Dyehouse No. 535 (Replaces No. 428). Procion Dyes: Application to Wool—**The dyeing behaviour and fastness characteristics of a wide range of both the cold-dyeing Procions and the "H" brands has now been determined. Determination of rate of uptake and rate of reaction with the fibre has shown that the "H" brands react much more slowly and it is essential that dyeing at the boil must be continued for at least 60 min. With both types, unreacted and/or hydrolysed dye on the fibre cannot be removed completely by any conventional aftertreatment and thus the very high intrinsic wet fastness is never realised in practice. With the "H" brands the presence of unreacted dye on the wool gives rise to staining of adjacent white cotton in fastness tests. The "H" brands are slightly more level dyeing than the more reactive types and initial uniform uptake of dye is essential. The addition of Lissolamine A50% and Lubrol W is still recommended for promoting level dyeing. Procion dyes are less level dyeing on wool than the best Carbolan dyes applied by the Carbolan Salt A method. Full, bright colours are possible on loose wool, slubbing, yarn, and knitted material but not, normally, on woven cloth. It is difficult to produce level dyeings of pale colours or tertiary mixtures. In contrast to the recommendation in the first edition, it is now stated that turquoise blues and bright greens are best produced with mixtures of Coomassie Turquoise Blue 3G and Procion Brilliant Yellow H5G. The former dye is

superior in dyeing behaviour to Procion Brilliant Blue H7G and dyeings of it are fully equal in fastness to those obtained with the reactive dye.

**Dyehouse No. 536. Wool Dyes: Effect of the W.I.R.A. Peroxy Acid/Sodium Hypochlorite Shrink-resist Finish on Shade and Wash Fastness—**The results tabulated in this note were obtained using a cold, slightly acid solution containing 0.03% of peroxy acid and an amount of hypochlorite equivalent to 0.06% available chlorine (calc. on wt. of soln.), followed by a cleaning treatment in an acid solution of sodium bisulphite and thorough rinsing. It is noted that a wide range of dyes are available which are unaffected in hue and do not show a serious reduction in wash fastness. In certain cases it is possible to dye the treated wool but the same reduction in wash fastness will be found compared with dyeings on untreated wool and the treatment must be perfectly uniform to ensure level dyeing.

**Dyehouse No. 537. Bleachability of Dyed Paper "Broke"—**Details are given of the ease with which papers dyed with the dyes listed in the pattern card, *Dyestuffs for Paper*, may be bleached. Such information helps in the selection of easy-bleaching dyes and thus minimises the problem of re-using "broke" and also serves as a guide for the selection of dyed "broke" for particular grades of paper.

**Dyehouse No. 538 (Replaces No. 431). Dyeing of Courteille Acrylic Fibre with Disperse Dyes—**The fastness to light, washing, perspiration, and steaming of dyeings of selected disperse dyes and mixtures of them have been determined. The suitability of individual dyes for (1) dyeings having maximum light fastness, (2) dyeings of the highest fastness to light and pleating, and (3) dyeings in full depths where fastness to heat or light is not necessarily of first importance.

**Dyehouse No. 540 (Replaces No. 498). Procion Brilliant Blue H7G: Dyeing of Cellulosic Fibres by Batchwise and Pad-Roll Procedures—**Revised methods are given. The preferred alkali to use with viscose rayon is a 4:1 mixture of sodium carbonate and sodium hydroxide. Since non-ionic agents promote aggregation of dye and may lead to speckly dyeings, it is emphasised that products such as Lissapol N should not be added to the dyebath.

**Dyehouse No. 541. Procion Dyes: Application to Chlorinated Wool/Cellulosic Fibre Blends—**It has been found that by adding Perminal BX or Calsole Oil HS to the dyebath the amount of Procion dye absorbed by the chlorinated wool can be reduced without affecting the fixation of dye on the cellulosic fibre. The optimum amounts of these products to use with particular dyes are tabulated and details are given of batch-wise and semi-continuous dyeing methods.

**Dyehouse No. 543. Procion Dyes: Dyeing of Ribbons, Tapes and Narrow Fabrics by the Pad (Alkali)-Batch (Cold) Process—**The value of this procedure—extensively used for standard width materials—for dyeing narrow fabrics has been studied. Deep dyeings of high wet fastness are obtainable and the method is more economical in plant and may well be superior in producing solid dyeings on narrow fabrics with heavy (e.g. head) or tightly woven selvages.

#### James Robinson & Co. Ltd.

**CHROMOL COLOURS—**This card contains dyeings in two depths on wool slubbing of eight chrome dyes applied by both the single-bath and afterchrome methods. Colours include a yellow, an orange, four browns, an olive, and a black. The Chromol Black T is only to be dyed after-chrome but gives dyeings having a fastness to light of 8 in 2 × normal depth, alkaline milling 4-5 (staining of white wool) and 5 to potting.



**Reactive dyestuffs**

**for padding cellulosic fibres**

**Details overleaf**



**® Drimarene-4**

**SANDOZ PRODUCTS LTD BRADFORD**

# <sup>®</sup> Drimarene-y

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K. W. Marim and A. Wissing

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(in English)

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**Apparatus for Coating Thin Self-sustaining Tubular Films**

Union Carbide Corpn.

BP 829,016

Printing Tufted Fabrics (IX p. 325)

Spraying Liquids or Solids on to Paper, Cloth, etc. (X p. 327)

**II—WATER AND EFFLUENTS****PATENT****Silica Sol as a Coagulant in Water Treatment**

Water Research Assocn.

BP 827,586

Silica sol obtained by acidifying sodium silicate with an Al or Fe salt, e.g.  $Al_2(SO_4)_3$  or  $FeSO_4$  and  $FeCl_3$ , is used as a coagulant in water treatment, being continuously prepared by mixing solutions of the two components. By using  $Al_2(SO_4)_3$  in this as well as in its normal capacity as a coagulant, use of additional chemicals, e.g. strong mineral acids or  $NaHCO_3$ , may be avoided.

C.O.C.

**III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS****Relationships between Metal Complex Stability and the Structure of the Complexing Agents**

G. Schwarzenbach

Anal. Chem., 32, 6 (Jan 1960)

A survey of complexing agents and the factors affecting complex stability covering the following subjects: the tendency of metal ions to co-ordinate and their electrovalent character; general and selective tendencies of ligand atoms to complex formation; the chelate effect, size and strain of the ring; multidentate ligand efficiency and structure; stereochemistry of complexes and specific chelating action.

P.B.S.

**Complexones. IV—trans-1,2-Diaminocyclohexene- and 1-Phenylethylenediamine-N,N,N',N'-tetraacetic Acids**

V. G. Yashunskii, V. F. Vasil'eva, L. I. Tikhonova, and M. N. Shehukina

Zhur. obshch. khim., 29 (Aug 1959) 2709-2712

Preparation of two new complexing agents, trans-1,2-diaminocyclohexene-(4)- (I) and 1-phenylethylenediamine- (II) tetraacetic acids is described. The complexing powers of I and II compare favourably with EDTA.

G.J.K.

**Pyridine Derivatives as Complex Components. I—Pyridine Carboxylic Acids**

G. Anderegg

Helv. Chim. Acta., 43 (1 Feb. 1960) 414-424

An investigation is reported of the complexes of the anions of picolinic acid, 6-methyl-picolinic acid, and dipicolinic acid with the 15 metallic cations H, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Ag, Hg. A new possibility of using a copper amalgam electrode ( $pCu$ -method) for studying complexes of metals other than copper is described. Despite the low basicity of their anions, the pyridine carboxylic acids form metal complexes of remarkably high stability, and a possible explanation of this fact is proposed.

H.H.H.

**Complexones. XXXI—N-(o-Hydroxycyclohexyl)-ethylenediamine-N,N',N'-triacetic Acid (OETA)**

J. Schubert, G. Anderegg, and G. Schwarzenbach

Helv. chim. Acta, 43 (1 Feb 1960) 410-413

OETA is investigated as a complexing agent for the 7 metallic cations  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$ ,  $Fe^{3+}$  by different methods. The stability constants of the complexes are compared with those of ethylenediamine- and hydroxyethylenediamine-tetraacetic acid which do not possess the cyclohexane ring. The latter is found to exert considerable stabilising effect.

H.H.H.

**Alkaline Degradation of Alginates**

R. L. Whistler and J. N. BeMiller

J. Amer. Chem. Soc., 82 (20 Jan 1960) 457-459

Alginic acids, esters, and salts are readily degraded by alkaline solns. at 80-120°C. with formation of new 6-carbon dicarboxylic saccharinates, i.e. 3-deoxy-2-C-hydroxy-methyl-pentariates.

F.J.

**Tris(ethylenediamine)cadmium Hydroxide, a Colourless Aqueous Solvent for Cellulose**

G. Jayme and K. Neuschäffer

Naturwissenschaften, 44 (1957) 62-3

Chem. Abs., 53 (25 Nov 1959) 22906

Basic  $CdCl_2$  solution is treated at 0°C. with 20-35% ethylene diamine solution to yield Cadoxen (soln. of tris(ethylenediamine)cadmium hydroxide). Cadoxen containing 6-5% Cd and 27-9% ethylenediamine solution dissolved 4-5-5-0 wt. % of rayon (degree of polymerisation 670) giving a clear solution at room temperature. Slaking  $CdO$  with 30% ethylenediamine solution for 15 min. at room temperature, followed by centrifuging, gives a solution containing 4-5% of Cd and capable of dissolving 3% of cellulose.

C.O.C.

**PATENTS****Ester Type Surfactants and Detergents**

General Aniline

USP 2,898,352

A mixed anhydride of a fatty acid and boric acid is treated with a water-soluble hydroxyalkane sulphonate with formation of 1 mole boric acid for each 3 moles ester produced. The products are excellent detergents.

C.O.C.

**Improving the Foaming of Synthetic Detergents**

General Aniline

BP 829,701

The generation of foam by synthetic detergents and its stability are much improved by presence of a non-ionic surface-active N-polyoxyethylenated alkylated benzenesulphonamide of > 7 C and containing 20-50% by wt. of combined ethylene oxide, e.g. dodecylbenzenesulphonamide combined with 4 mol. ethylene oxide.

C.O.C.

**Increasing the Foam Stability of Organic Sulphate and Sulphonate Detergents**

Shell Development Co.

USP 2,900,346

Monoethers of glycerol and monohydric aliphatic saturated alcohols having a straight hydrocarbon chain of 8-16 C and in which the OH group is attached to the last or penultimate C atom of the chain, e.g. n-decylglycerol monoether, have no foaming power by themselves but added to organic sulphate and sulphonate detergents of all kinds they much increase the foam stability of the detergents.

C.O.C.

**Carboxylic Esters of Sucrose or Raffinose—Detergents**

Sugar Research Foundation

BP 824,654

Sucrose or raffinose is heated with an ester of a resin acid or fatty acid of 6-30 C and a non-saccharide alcohol at 20-180°C. in presence of an alkaline catalyst and a solvent. The products are excellent detergents and emulsifying agents having all the advantages of non-ionic surfactants.

C.O.C.

**Emulsifying Agents**

Dehydag, Deutsche Hydrierwerke

BP 827,536

Salts of high mol. wt., straight chain, aliphatic or cycloaliphatic amines with polycarboxylic acids, e.g. hexadecylaminemalonate, are excellent emulsifying agents for mineral oils or other organic liquids of low viscosity.

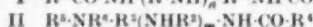
C.O.C.

**Auxiliary Agents obtained from  $\gamma$ -Lactones and Polyamines**

General Aniline

BP 828,665

Treating  $\gamma$ -lactones with polyamines yields compounds of formula—



( $R^1$  and  $R^4$  = a  $\gamma$ -hydroxyalkyl of 3 or 4 C;  $R^2$  and  $R^3$  = alkylene of 2-4 C;  $R^5$  = Alk, alkenyl or hydroxyalkyl of 1-20 C;  $R^4$  = H, Alk or hydroxyalkyl of 1-20 C;  $n$  = 1-4;  $m$  = 0-4) depending on the components used. The products are water-soluble and have a very wide range of uses as auxiliary agents and as intermediates for finishing agents.

C.O.C.

**Rendering Textiles Antistatic and Readily Wettable**

Dexter Chemical Corpn.

BP 828,012

The textiles are treated with a composition made up of (1) a water-dispersible hydroxyamine containing a  $C_8$ - $C_{24}$  hydrocarbon group directly attached to the amine N and (2) a water-soluble non-volatile polyhydric alcohol. The amine forms 50-95% by weight of the mixture.

C.O.C.

**Antistatic Finish for Textiles**

Doering Milliken Research Corp.

USP 2,901,451

The water-soluble product obtained by treating a dicarboxylic unsaturated acid, e.g. maleic acid, with excess of a polyglycol compound, e.g. a polyethylene glycol ether of mol.wt. 950-1050, can be applied to textiles from an aqueous bath and on exposure becomes cross-linked to give a resin insoluble in both water and organic solvents. They can therefore be used to give an antistatic finish which is fast to washing and dry cleaning.

C.O.C.

**Lubricant for Hydrophobic Filaments**

ICI

BP 828,735

A lubricant for filaments made from linear hydrocarbon polymers, particularly polypropylene, containing a major proportion of the polymer in isotactic form, consists of an aqueous solution of a polymer containing recurring oxyalkylene units; e.g. poly(ethyleneglycol) of average mol. wt. 300.

C.O.C.

**Catalyst for Aldehyde Resins**

Tootal Broadhurst Lee Co.

BP 827,645

Acid salts of polybasic acids having a first dissociation constant in water of  $< 10^4$  with a metal of which a less acid salt with the same polybasic acid is precipitated before the first mentioned acid salts on removal of water from the solution, can be used as catalysts for aldehyde resins without any of the disadvantages hitherto attaching to the use of acid catalysts. Twenty-four examples of the use of these catalysts for widely different uses of aldehyde resins are given and there are 33 claims.

C.O.C.

**Modified Aminoplast Resins—Textile Assistants and Coating Agents**

Chemische Fabrik Pfersee

BP 827,469

Thermosetting basic condensates insoluble in water but readily soluble in dilute aqueous acid and in non-polarised or weakly polarised organic solvents are obtained by heating an aminoplast-forming N compound with paraformaldehyde, an oxyalkylamine and an aliphatic monocarboxylic acid of  $> 10^\circ\text{C}$  or an abietinic acid under anhydrous conditions. The products, e.g. that obtained from stearic acid, melamine, paraformaldehyde, ethanolamine, and ethanol, are useful as textile assistants and coating agents. They have hydrophilic and emulsifying properties but on being hardened lose these properties and become hydrophobic.

C.O.C.

**Modified Aminoplast Resins—Water-repellent Agents**

Chemische Fabrik Pfersee

BP 827,468

Urea or an aminotriazine and paraformaldehyde are mixed with either (1) a saturated or monoethylenically unsaturated aliphatic monocarboxylic acid of  $> 10^\circ\text{C}$  or abietic acid, or (2) an unsubstituted aliphatic monohydric alcohol of  $1-4^\circ\text{C}$ , and then heated. The resulting condensates are wax like and melt at  $40-65^\circ\text{C}$ . They are insoluble in water or dil. acid but readily soluble in non-polarised or only slightly polarised organic solvents. They are used as impregnating and film-forming agents and are particularly suitable for imparting a water-repellent finish to textiles.

C.O.C.

**Thiourea Dioxide (C.I. Reducing Agent 11)**

S. A. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny &amp; Ciry

BP 828,907

Thiourea dioxide is made by passing a gas containing ozone into a solution or dispersion of thiourea.

C.O.C.

**Antifungal Composition**

Établissements Sargent Laboratoires Prolac

BP 827,434

Oxygenated acids and anhydrides of boron or their salts and esters are mixed with an organic compound containing in  $\alpha$ - and  $\beta$ -positions to one another two identical or different radicals chosen from OH, NH<sub>2</sub>, and NH. There are 0.2-5.0 mol. organic compound per mol. boric anion. The mixture is then brought to  $< \text{pH } 9$ . The mixture exhibits synergistic antifungal properties. Such compositions have wide uses, e.g. in water paints and emulsions.

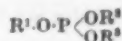
C.O.C.

**Light Stabiliser for Halogeno Resins**

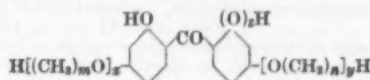
Monsanto Chemical Co.

BP 828,712

A mixture of a compound of formula—



(R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> = hydrocarbon groups of 4-14 C free from olefinic unsaturation) and one of formula—



(m, n, x, y, and z = 0 or 1)

e.g. triphenyl phosphate and 2-hydroxy-4-methyl benzophenone, is excellent for stabilising halogeno resins, particularly poly(vinyl chloride), to light.

C.O.C.

Rendering Proteins Resistant to Putrefaction (V p. 320)

Mercerising and Wetting Agents (VII p. 322)

Pinonic Acid as a Mercerising Penetrant (VII p. 322)

Flame-resisting Cellulosic Textiles by use of Phosphorus Triisocyanate or Phosphoryl Triisocyanate (X p. 327)

Bromate- or Chlorite-urea Oxidative Fixing Composition for Setting Keratinous Fibres (X p. 327)

Myrobalans (C.I. Natural Brown 6)—an Important Tanning Material (XII p. 328)

Compositions for Removing Hair or Wool from Skins (XII p. 329)

**IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS****How Much Research? A Critical Problem in the Manufacture of Textile Dyes**

G. S. J. White

J.S.D.C., 76 (Jan 1960) 16-22

**Electron Gas Theory of Colour of Natural and Artificial Dyes**H. Kuhn *Fortschr. Chem. org. Naturstoff* (L. Zechmeister, editor, Springer-Verlag) 17 (1959) 404-451

Review, with many references.

C.O.C.

**Metastable State of Dye Molecules: Absorption Bands in the Visible Spectrum**

E. Laffitte and G. Nouchi

Compt. rend. 248 (1959) 2746-8

Chem. Abs., 53 (25 Nov 1959) 22957

The absorption spectrum between 400-700 mμ. was measured of solutions in plexiglas of Fluorescein (C.I. 45350), Rhodamine B (C.I. 45170), Trypanflavine, Acridine Orange (C.I. 46005), Methyl Violet (C.I. 42535), and Malachite Green (C.I. 42000) at  $-180^\circ\text{C}$ . The absorption was increased by cooling. Slight deformation of the absorption curves occurs in direction of shorter wavelengths. The shoulder in the absorption curve is attributed to the metastable state of the molecule. It can be transformed into distinct absorption bands by introducing a reference sample of adjusted optical d.

C.O.C.

**Radiation Chemistry of Organic Dyes**

W. H. Cropper

U.S. At. Energy Comm. SCTM 139-59 (16), 32 pp. (1959)

Chem. Abs., 53 (25 Nov 1959) 21088

Review, 37 references.

C.O.C.

**Syntheses of 4-Hydroxy Derivatives of  $\beta$ -Apo-carotinals and  $\beta$ -Apo-carotinic Acids, together with the Preparation of 3,4-Dehydro- $\beta$ -apo-carotinals and 3,4-Dehydro- $\beta$ -apo-carotinic Acids. XXVIII—Carotenoid Syntheses**

R. Entschel and P. Karrer

Helv. chim. Acta, 43 (1 Feb 1960) 94-101

The general method previously described (cf. XXVII, *ibid.*, 42 (1959), 466) has now been successfully used for the syntheses of 4-hydroxy- $\beta$ -apo-8'-carotinal (C<sub>39</sub>), 3,4-dehydro- $\beta$ -apo-8'-carotinal (C<sub>39</sub>), 4-hydroxy- $\beta$ -apo-8'-carotinic acid (C<sub>39</sub>) and its methyl ester, 3,4-dehydro- $\beta$ -apo-8'-carotinic acid (C<sub>39</sub>) and its methyl ester, 4-hydroxy-15,15'-dehydro- $\beta$ -apo-8'-carotinal (C<sub>39</sub>), 3,4; 15,15'-dehydro- $\beta$ -apo-8'-carotinal (C<sub>39</sub>), 4-hydroxy-15,15'-dehydro- $\beta$ -apo-carotinic acid (C<sub>39</sub>) and its methyl ester, and 3,4; 15,16'-dehydro- $\beta$ -apo-8'-carotinic acid (C<sub>39</sub>) and its methyl esters. Preparative details are given.



### Spectrophotometric Testing in a Series of Carotenoid Dyes

B. G. Savinov *Primenenie Metodov Spektroskopii v Prom. Proizvodstven. Tovarov i Sel'sk. Khoz., Leningrad. Gosudarst. Univ. im. A. A. Zhukovskogo Materialy Soveshchaniya, Leningrad (1955) 136-144 Chem. Abs., 54 (10 Jan 1960) 626*

In a series of carotenoid dyes the structure of particular cis-trans isomers could be closely approximated as a result of the dependence of their spectrophotometric characteristics on their stereo configuration. C.O.C.

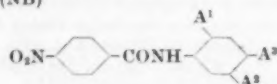
### Counter-polarised Systems and Colour

V. A. Izmail'skii and A. V. Mal'gina

#### I—Spectra of Some Derivatives of 4-Nitrobenzanilide having several Electrophobic Chromophores in one Nucleus

*Zhur. obshch. khim., 29 (Aug 1959) 2623-2630*

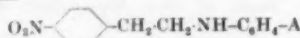
The effect of two electrophobic groups in para position with respect to each other on the absorption (200-450 mμ.) and reflection (400-700 mμ.) spectra of 4-nitrobenzoyl-arylamides (NB)



(A<sup>1</sup> and A<sup>2</sup> = H, CH<sub>3</sub>, OCH<sub>3</sub> or OC<sub>2</sub>H<sub>5</sub>; A<sup>3</sup> = H, NHCOC<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OH or N(CH<sub>3</sub>)<sub>2</sub>) has been studied. A strong bathochromic shift occurs when A<sup>1</sup> = A<sup>2</sup> = OCH<sub>3</sub> resulting in formation of a second absorption band (λ<sub>max</sub> = 320-355 mμ.) in the case of 4'-nitro-2,5-dimethoxy benzanilide. The effect of the [1-CONH, 2,5-(OCH<sub>3</sub>)<sub>2</sub>] system is very close to that of [1-CONH, 4-OCH<sub>3</sub>]. Experimental details for the preparation of 13 different NB are given.

#### II—Absorption Spectra of some Derivatives of N-[β-(4-nitrophenyl)-ethyl]-aniline having Electrophobic Chromophores in para- and meta-Positions

V. A. Izmail'skii and V. E. Limanov *Ibid., 2631-2638*  
Ten derivatives of N-[β-(4-nitrophenyl)-ethyl]-aniline of formula—



(A = CH<sub>3</sub>, OCH<sub>3</sub>, OH, NHCOC<sub>2</sub>H<sub>5</sub> or NH<sub>2</sub> para or meta position to the NH) have been prepared and their reflection spectra (400-700 mμ.) measured. Presence of A in para position (PP) causes a greater bathochromic effect compared with the meta position (MP). The order of increasing bathochromic shift for PP is: H, CH<sub>3</sub>, OCH<sub>3</sub>, NHCOC<sub>2</sub>H<sub>5</sub>, OH, NH<sub>2</sub>, whilst for MP it is surprisingly: H, OCH<sub>3</sub>, NH<sub>2</sub>, NHCOC<sub>2</sub>H<sub>5</sub>, OH (400-500 mμ.), and H, NHCOC<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, OH (550-700 mμ.). G.J.K.

### Separation Component in the Synthesis of Organic Dyes

#### VI—Behaviour of the Naphthalene-1,5-disazo System

I. Reichel and A. Balint

*Acad. rep. populare Romine, Baza cercetării științ. Timișoara, Studii cercetări științ. Ser. I, 4 (1957) 33-49*

The naphthalene-1,5- and -1,4-disazo systems are adequate separation components when synthesising asymmetric azo dyes. Green dyes are prepared by introducing yellow and blue components into the system. Salicylic acid, 1-phenyl-3-methyl-5-pyrazolone, and acetoacetic anilide are used as yellow components and 1,8-aminonaphthol-2-(4-nitrophenylazo)-3,6-disulphonic acid (I) as the blue component. Best results are got by incomplete diazotisation of 1,5-bis-(sulphoamino)naphthalene (II), coupling with 1-phenyl-3-methyl pyrazolone or with acetoacetic anilide, diazotising the second sulphoamino group and finally coupling with I.

#### VII—Absorption Spectra of Azo Dyes having Naphthalene-1,5- and 1,4-disazo as the Central Components

*Ibid., 51-63*

*Chem. Abs., 54 (25 Jan 1960) 1854*

Comparative study of the absorption spectra of asymmetric green and yellowish orange dyes of the naphthalene-1,5-disazo (III) and naphthalene-1,4-disazo (IV) series,

with those of combination of the yellow and blue components and with a mechanical mixture of them. The absorption spectra of III and IV are also compared with the spectrum of a similar dye not having the naphthalene-disazo central component. Presence of III and IV in the centre of the molecules results in the intramolecular optical mixing of the coloured end components. The independent behaviour of the end components in the asymmetric green dyes and in the symmetrical yellowish orange dyes is seen in the general shape of the absorption curves, in the position of the maximum, and in the intensity of absorption in certain characteristic spectral regions. The systems III and IV can be used as separation components when synthesising asymmetric azo dyes if appropriate end components are selected. C.O.C.

### The Remazol Linkage

E. Bohnert

*J.S.D.C., 75 (1959) 581-585*

#### Tartrazine (C.I. Food Yellow 4) BS 3211:1960

British Standards Institution. Price 3/-

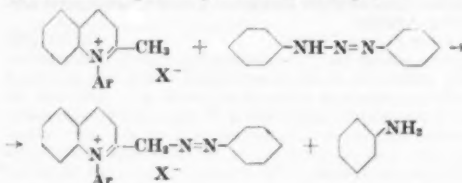
Applies to Tartrazine for use as a food dye. Limits are specified for matter volatile at 135°C., matter insoluble in water, di-isopropyl ether extract, subsidiary dyes, phenylhydrazine-p-sulphonic acid, chloride and sulphate, dye content, copper, arsenic, lead, and heavy metals (as sulphides). C.O.C.

### Synthetic Dyes. XII—Synthesis of Monoazo-N-Aryl Quinaldinium Salts

G. T. Pilyugin and S. V. Shinkorenko

*Zhur. obshch. khim., 29 (Aug 1959) 2760-2763*

Treating quaternary salts of N-aryl quinaldine with diazonium compounds yields monoazo dyes—



(Ar = C<sub>6</sub>H<sub>5</sub> or p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup> or I<sup>-</sup>). Six such dyes have been prepared and their absorption spectra (400-650 mμ.) determined. G.J.K.

### Derivatives of Triazine. I—Substantive Triazine Azo Dyes

V. I. Mur *Zhur. obshch. khim., 29 (July 1959) 2267-2271*

Five new green azo dyes (AD) based on 2-(4'- and 2'-methoxy- and 2'-hydroxyphenyl)-4,6-dichloro-1,3,5-triazines, have been prepared and the absorption spectra (visible range) of their aq. soln. (pH 6-6.5) determined. The investigation of AD and of their analogues, based on 2-phenyl-4,6-dichloro-1,3,5-triazine and cyanuric trichloride (whose third chlorine atom has been substituted by the aniline grouping) has revealed a weak hypsochromic effect caused by the imino group between triazine and phenyl. G.J.K.

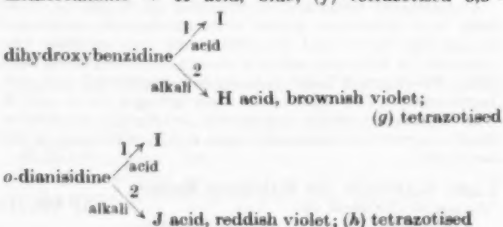
### Dyes derived from p-t-Butylaniline

T. Endo and K. Shimada

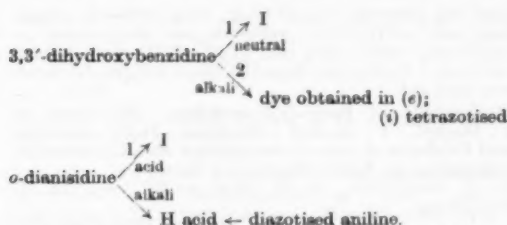
*Shinshu Daigaku Sengakubu Kenkyu Hokoku, 8 (1958) 130-2*

*Chem. Abs., 54 (10 Jan 1960) 902*

Preparation of the following dyes substantive to Vinyon and nylon is described: monoazo dyes, (a) p-t-butyl-aniline (I)  $\xrightarrow{\text{alkali}}$  J-acid, orange; (b) I  $\xrightarrow{\text{alkali}}$  H acid, reddish violet, (c) H acid  $\xrightarrow{\text{acid}}$  I, pale brown; (d) 1-amino-2-naphthol-4-sulphonic acid  $\rightarrow$  I, yellow; (e) I  $\rightarrow$  2,5-dichloroaniline  $\rightarrow$  H acid, blue; (f) tetrazotised 3,3'-







C.O.C.

**Synthesis of Reactive Dyes for Cellulose**

O. Manabe, S. Kitahara and H. Hiyama

*Kogyô Kagaku Zasshi*, **61** (1958) 89-92*Chem. Abs.*, **53** (25 Nov 1959) 22958

Dyes containing the 2,4-dichloro-1,3,5-triazinyl radical have been prepared. Thus coupling diazotised metanilic acid (0.05 mole) with H acid (0.05) in the 2-position in presence of  $\text{Na}_2\text{CO}_3$  (15 g.) in ice by stirring for 3 hr. yielded a monoazo compound (28 g.). This compound (5.5 g.) was dissolved in aq.  $\text{NaHCO}_3$  and treated with cyanuric chloride (1.85 g.) in acetone at 2-5°C. for 1.0-1.5 hr. to yield a red dye (6 g.). Similarly the monoazo dye, obtained by coupling diazotised sulphanilic acid with o-anisidine in para position, gave a yellow dye when treated with cyanuric chloride. A reactive orange dye was prepared from diazotised m-nitro-aniline coupled with G acid in the 1-position, reduced and treated with cyanuric chloride; an orange brown dye was prepared by coupling H acid with 1-naphthylamine-8-sulphonic acid in the 4-position and treating with cyanuric chloride. All four dyes on cotton had very good fastness to washing and light. Their dichlorotriazinyl radical is believed to combine chemically with the hydroxy group of cellulose.

C.O.C.

**Yellow Pigments from Aminophenylimides of Naphthalic Acid**

B. M. Krasovitskii, E. E. Khotinskaya, N. D. Ogdanets and E. M. Alenich

*Uchenye Zapiski Khar'kov. Gosudarst. Univ.*im. A. M. Gorkogo, **71**, *Trudy Khim. Fak. i**Nauch.-Issledovatel. Inst. Khim.* No. 14 (1956) 253-4*Chem. Abs.*, **53** (25 Nov 1959) 22988

Yellow pigments were obtained by condensing p-aminophenylimide and naphthalic acid m-aminophenylimide respectively with 2,4-dinitrobenzene. They are insoluble in water, alcohol, weak acid, and alkali, slightly soluble in acetone, benzene, and butyl acetate. They resemble existing yellow pigments in fastness to light but are inferior in purity of hue.

C.O.C.

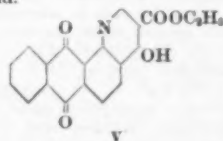
**Cellulose Acetate Dyes. I—Synthesis of Amino-anthraquinonyl Acrylates and Pyridinoanthraquinones**

K. Sirasankaran, K. S. Sardesai, and S. V. Sunthakar

*J. Sci. Ind. Research (India)* **18B** (1959) 164-8*Chem. Abs.*, **54** (25 Jan 1960) 1518

1-Aminoanthraquinone (2.23 g.), diethylethoxymethylenemalonate (2.10) and xylene (20 ml.) refluxed for 4 hr., the xylene distilled in vacuo, the residue extracted with benzene at room temperature and the benzene distilled off gave a 92% yield of the reddish yellow diethyl 1-anthraquinonylaminoethylenemalonate (I). The following were similarly prepared (% yield and colour given): 2-anthraquinonylaminoethylenemalonate, 83, orange; diethyl 1,5-dianthraquinonylaminoethylenemalonate (II), 77, yellowish orange; diethyl 1,4-dianthraquinonylaminoethylenemalonate, 60, reddish violet; diethyl 4-methoxy-1-anthraquinonylaminoethylenemalonate (III), 78, reddish orange; and diethyl 4-hydroxy-1-anthraquinonylaminoethylenemalonate (IV), 56, reddish violet. I (0.65 g.) and diphenylether (8 ml.) refluxed 45 min., cooled, diluted with petroleum ether (15 ml.) precipitated the yellowish red 4'-hydroxy-3'-carbethoxy-1,2-pyridinoanthraquinone (V) in 77% yield. II similarly cyclised gave 95% of the red 4',4''-dihydroxy-3',3''-dicarbethoxy-1,2,5,6-dipyridinoanthraquinone. When IV was similarly cyclised the expected anthraquinone was not obtained but a compound of unknown structure (72.2% C, 5.0% H). III cyclised gave a 29% yield of the reddish orange 4-methoxy-4'-hydroxy-3'-carbethoxy 1,2-pyridinoanthraquinone. V (1 g.) and 10%

alcoholic KOH (20 ml.) heated for 7 hr. in a water bath, the alcohol removed and the mixture cooled and neutralised with 10% HCl precipitated the yellow 4'-hydroxy-3'-carbethoxy-1,2-pyridinoanthraquinone in 65% yield. VI (0.4 g.) and dibutyl phthalate (6 ml.) refluxed 20 min., cooled and diluted with petroleum ether (15 ml.) precipitated a 92% yield of the brown 4'-hydroxy-1,2-pyridinoanthraquinone. I and V had good affinity for and fastness on cellulose acetate. All these dyes have satisfactory fastness to sublimation and gas fume fading. Fastness to gas fume fading was improved by lowering the basicity of the  $\text{NH}_2$  and fastness to light by having the basic N in the leuco nucleus to curb the electron mobility in the compound.



C.O.C.

**Disperse Dyes. XVII—1-Hydroxy-4-arylamino-anthraquinones and 1-Amino-4-arylaminoanthraquinones**

K. Naiki, E. Cho, and S. Tsuruoka

*Yûki Gôsei Kagaku Kyôkai Shi* **17** (1959) 705-710*Chem. Abs.*, **54** (25 Jan 1960) 1853

1-Hydroxy-4-chloroanthraquinone (2 g.) treated with aniline (24), K acetate (3), and Cu acetates (0.03 g.) gives a 76% yield of the violet 1-hydroxy-4-anilino anthraquinone. The following were similarly prepared: 1-hydroxy-4-(p-toluidino)anthraquinone, 1-hydroxy-4-(m-hydroxymethylaminilino)anthraquinone, both being violet. 1-Amino-4-methoxyanthraquinone (0.5 g.) and aniline (4.1) were heated together for 24 hr. at 150-160°C., washed with 2% HCl, then water added. The product was dissolved in benzene, absorbed in a column of  $\text{Al}_2\text{O}_3$ , developed with benzene and the blue zone extracted with hot alcohol to give a 63% yield of the violet 1-amino-4-anilinoanthraquinone. The bluish violet 1-amino-4-(p-toluidino)anthraquinone and the violet 1-amino-4-(m-hydroxymethylaminilino)anthraquinone were similarly prepared. Leucoquinizarin (2), aniline (20), acetic acid (2), and  $\text{H}_3\text{BO}_3$  (1.2) were heated for 8 hr. at 120-130°C., cooled, washed with 3% HCl (200 cc.) and dried to give a 68% yield of the violet 1,4-dianilinoanthraquinone. The violet 1,4-di-p-toluidinoanthraquinone and the blue 1,4-bis(m-hydroxymethylaminilino)anthraquinone were similarly prepared. The affinity of these dyes for polyester fibres and the fastness of their dyeings are given.

C.O.C.

**The Solubilities and Heats of Solution of Disperse Dyes in Water**

D. Patterson and R. P. Sheldon

*J.S.D.C.*, **76** (March 1960) 178-181**Electron-microscope Examination of the Effect of Boiling Water on Some Anthraquinone Vat Dyes**

D. G. Drummond and J. O. Warwicker

*J. Textile Inst.*, **50** (Aug 1959) T 487-493

Boiling a freshly precipitated anthraquinone vat dye in water increases the general size of the particles to an extent dependent on the dye. Of the dyes used only 6,15-dimethoxyisoviolanthrone changed its crystal habit under the treatment.

C.O.C.

**X-Ray Study of the Polymorphism of Some Anthraquinone Vat Dyes**J. O. Warwicker *J. Textile Inst.*, **50** (July 1959) T 443-7

Comparison of the X-ray powder photographs of different samples of each of 10 anthraquinone vat dyes shows that polymorphism is a common phenomenon with these dyes.

C.O.C.

**Spectroscopy and Photochemistry of Cellulose-tendering Dyes**

E. W. Abrahamson, I. Panik, and K. V. Sarkanen

*Proc. Cellulose Conf. Ind., Syracuse*, (1959) 127-141*Chem. Abs.*, **54** (10 Jan 1960) 902

An O-free solution of the dye under examination ( $3.3 \times 10^{-4}$  M.) in a glass-forming solvent consisting of tetrahydrofuran:ether:isopentane:alcohol (4:4:3:5 by vol.) was prepared in a 1-cm. glass cell, frozen to a rigid, transparent glass in a liquid-air thermostat, irradiated

with a 100 w. Hg arc, and the absorption spectra observed. Spectral changes occurring during irradiation indicated presence of a dye semiquinone and its corresponding negative ion. To study the semiquinone intermediates in di-Na 2,7-anthraquinonedisulphonate (I) in aqueous and semiaqueous medium by flash photolysis, two quartz flash tubes filled with Xe and connected to a high-voltage capacitor were mounted inside a reflector tube with a thermostatted cell containing the solution to be examined. Light from a Zr arc was passed through the cell and focused on a grating monochromator. Rapid changes in light transmission at any wavelength were detected and recorded by a multiplier photo tube and oscilloscope. When aqueous, degassed I solution was flash illuminated there was initial rapid decrease in absorption at 505 mμ, followed by much slower decay because of the semiquinone negative ion. In presence of O, the 508 mμ. peak was markedly quenched because the free radical reacted with O. I in 0.001 M-H<sub>2</sub>SO<sub>4</sub> containing 20% alcohol showed a semiquinone absorption band at 390 mμ., in conc. H<sub>2</sub>SO<sub>4</sub> absorption changes were negligible. It is the excited  $\pi$ - $\pi^*$  singlet state which is photochemically active in anthraquinone vat dyes and the predominant factor in determining the tendering action of a dye is the relative positions of the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  excited states of the dye. The low tenderers have strongly basic groups on the ring, and these appear the more effective the closer they are to the CO group. Most non-tendering anthraquinone vat dyes will have  $n$ - $\pi^*$  levels lying at higher energy levels than the  $\pi$ - $\pi^*$ . C.O.C.

#### Pyrrrole-quinone Dyes

H. Fischer, A. Treibs, and E. Zaucker

*Chem. Ber.*, **92** (1959) 2026-9  
*Chem. Abs.*, **54** (10 Jan 1960) 901

Present knowledge of the mechanism of the reactions of pyrroles and formation of pyrrole dyes suggests that the pyrrole-quinone dyes are dipyrrolylquinones. C.O.C.

#### Dichroism of Pyrazolinone Dyes in Stretched Poly(vinyl Alcohol) Sheets

H. Ono, Y. Tanizaki and I. Tanaka

*Nippon Shashin Gakkai Kaishi*, **21** (1959) 115-120

Pyrazolinone azomethine dyes have two absorption maxima in the visible region; these maxima can be displaced by changing the nature of the radicals substituted in the 3-C and 1-N atoms. To determine the origin of the bands measurements were made using polarised light of the absorption spectra of stretched sheets of poly(vinyl alcohol) dyed with the K salts of 4-(*p*-dimethylamino)-phenylimino-3-methyl-1-(*p*-sulphophenyl)-5-pyrazolinone and 4-(*p*-dimethylamino)benzylidene-3-methyl-1-(*p*-sulphophenyl)-5-pyrazolinone. The sheets had a mean degree of polymerisation of 1500. Layers 0.2 mm. thick were soaked in the dye liquors, dried, and stretched at 70-80°C. The dichroic spectra obtained are presented as graphs. Analysis of the absorption spectra indicates that the two absorption bands arise from two absorption systems, that responsible for the long wave absorption being oriented in the direction of elongation in the stretched film. Comparison with scale models suggested that the long wave band is associated with the chain connecting the dialkylamino-N and the carboxyl-O, and the short wave band with that connecting the dialkylamino-N and the 2-N of the pyrazolinone ring. This is in opposition to the findings of Brown and his colleagues (*Chem. Abs.*, **45** (1951) 5408). C.O.C.

#### Thioindigoid Dyes from 3-Aryl-2-arylimido-4-thiazolidinones

R. P. Rao

*Chem. Ber.*, **92** (1959) 2600-1  
*Chem. Abs.*, **54** (25 Jan 1960) 1854

A series of 5-(2-oxo-3-indolylidene)-3-aryl-2-arylimino-4-thiazolidinone dyes was prepared by condensing 3-aryl-2-arylimino-4-thiazolidinones with isatin. Isatin (0.06), a 4-thiazolidone (0.038-0.062 mole), Na acetate (10 g.), glacial acetic acid (50 cc.), and acetic anhydride (2-3 cc.) heated for 3-4 hr. at 150-160°C., poured into water (300-400 cc.), kept some time, filtered, the residue washed successively with water and dried, gave the following (Ar, colour of crystals, colour with conc. H<sub>2</sub>SO<sub>4</sub>): C<sub>6</sub>H<sub>5</sub>, brownish red, dark red; *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, dark red, dark reddish brown; *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, deep yellow dark red; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, red, dark red (in thin layers dark green); *o*-ClC<sub>6</sub>H<sub>4</sub>, light chocolate, dark red; *m*-ClC<sub>6</sub>H<sub>4</sub>,

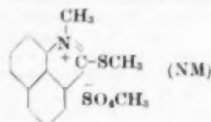
deep red, yellowish red; *p*-ClC<sub>6</sub>H<sub>4</sub>, deep yellowish orange, deep red; *o*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, yellowish red, deep violet; *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, violet, dark red; *p*-C<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>, deep orange, dark red; 1-C<sub>10</sub>H<sub>7</sub>, chocolate, chocolate; 2-C<sub>10</sub>H<sub>7</sub>, brownish red, dark red. C.O.C.

#### Derivatives of Benz-(c,d)-indoline. III—Salts of 1-Methyl-2-methyl-thiobenz-(c,d)-indoline and Products of their Condensation with Compounds containing an Active Methylene Group

N. S. Dokunikhin, G. M. Okaengendler, and Ya. B. Shteinberg

*Zhur. obshch. khim.*, **29** (Aug 1959) 2742-2745

N-methylthionaphthostyrene treated with dimethyl sulphate yields the corresponding quaternary salt (NM)—



Condensation of NM with cyanoacetic acid ethyl ester, acenaphthene or indoxyl leads to formation of disperse dyes. Their absorption spectra (400-700 mμ.) in *m*-xylene are given. G.J.K.

#### Colour and Exo-molecular Interactions. VIII—Absorption Spectra of Molecular Complexes of 9-(*p*-Dimethyl-N-styryl)-acridine with 10-Alkyl-9-methyl-acridinium salts

V. A. Izmail'skii and S. V. Dmitrienko

*Zhur. obshch. khim.*, **29** (June 1959) 1842-1850

The absorption spectra (250-850 mμ.) of alcoholic soln. of 9-(*p*-dimethyl-N-styryl)-acridine with 10-ethyl- and 10-benzyl-9-methyl acridinium chlorides and iodides have been studied, and the occurrence of an absorption max. at 610 mμ. observed. Complex formation on the basis of layer-like association of flat molecules with partial  $\pi$ -bonding perpendicular to the plane of the molecule is suggested. The stability of these complexes is superior to those of the quinoline and pyridine derivatives. G.J.K.

#### Synthesis and Acid-base Properties of some Derivatives of Malachite Green (C.I. 42000)

P. M. Zavlin

*Trudy Leningrad. Tekhnol. Inst. im. Lenostra*, **44** (1958) 6-10

R(*p*-dimethylamino benzene)<sub>2</sub>COH were prepared from RMgR and (*p*-dimethylaminobenzene)<sub>2</sub>CO dissolved in dimethylaminobenzene. Measurement of the hydrolysis constants showed that *ortho* substituent, both electrophilic and nucleophilic, reduced the value of the constants.

#### Dependence of the Absorption Spectrum of Malachite Green on the pH of the Medium

*Ibid.*, **11-13**

*Chem. Abs.*, **53** (25 Nov 1959) 21802-3

In the region pH 3.7-7.00 the ratio of the extinction coefficients at 618 and 430 mμ. remained constant. These absorptions are caused by a singly charged cation. At low pH the ratio dropped as a result of an increased amount of a doubly charged cation absorbing close to 430 mμ. C.O.C.

#### Vat Dyes from Pyrenic Acid

B. M. Krasovitskii, I. N. Pirogova, and S. V. Tsarenko

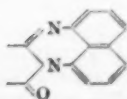
*Khim. Nauka i Prom.*, **4** (1959) 282-3

*Chem. Abs.*, **53** (25 Nov 1959) 21999

Condensing pyrenic acid (I) with *o*-phenylenediamine (II) or 1,8-naphthylenediamine (III) gave vat dyes containing two CO groups joined by a chain of conjugated bonds. They were readily vatted in weak alkali and can be used to dye wool as well as cotton. Thus heating I (2 g.) and II (1 g.) in glacial acetic acid (15 ml.) for 1 hr. at 80-90°C., filtering, washing with water, dil.-HCl, water, 10% Na<sub>2</sub>CO<sub>3</sub>, water and drying yielded 96% of—



which dyes cotton orange. Similarly I (2 g.) and III (1.5 g.) in glacial acetic acid (25 ml.) treated as above but the heating time being 2 hr., yielded 97% of—



which dyes cotton brown. Both dyes are soluble in conc.  $H_2SO_4$ , pyridine, and aniline. C.O.C.

**Thiazoles. XXXIX—Synthesis of Unsymmetrically Substituted 2,2'-Hydrazothiazoles and their Oxidation to 2,2'-Azothiazoles or Blue Thiazole Dyes**

E. Bulka, H. Beyer, and G. Brandenburg

*Chem. Ber.*, **92** (1959) 1447–1456

*Chem. Abs.*, **53** (25 Nov 1959) 21891

Describes preparation of 1-(4-methyl-5-carboxy-2-thiazolyl)thiosemicarbazide and its conversion with  $\alpha$ -halogenoketone to unsymmetrically substituted 2,2'-hydrazothiazoles. These on oxidation yielded either the corresponding 2,2'-azothiazoles or, if the 5-position in one of the thiazole rings was unoccupied, blue thiazole dyes. C.O.C.

**Synthesis of Thiazole Derivatives. XIII—Benzthiazolylthiazoles**

V. M. Zubarovskii

*Zhur. obshch. khim.*, **29** (June 1959) 2018–2027

Two new heterocyclic bases, 2-methyl-4- and 2-methyl-5-(benzthiazolyl-2'-yl)-thiazoles, have been prepared and their quaternary salts used in the synthesis of 8 polymethine dyes. The absorption max. of these dyes in ethanol are given. G.J.K.

**Synthesis of Thiazolidon Derivatives of Biological Interest. XII—Effect of some Substituents in the Molecules of Rhodanine Derivatives on Absorption Spectra in the Ultra Violet**

M. I. Ganitkevich and N. M. Turkevich

*Zhur. obshch. khim.*, **29** (June 1959) 2092–2096

The introduction of aryl or alkyl substituents ( $C_6H_5$ ,  $p$ - $C_6H_4OC_2H_5$ ,  $CH_3COOH$ ,  $CH_3COOC_2H_5$ ,  $CH_3COONH_4$ ,  $C_6H_5COONH_4$ ) in position 3 in rhodanine and its derivatives has practically no effect on the K-chromophores. An analogous observation was made for the product of the reaction of rhodanine with NaOH in alcoholic solution (NA). The reaction of NA with 5-arylidine rhodanines containing OH or  $NO_2$  in *ortho* or *para* positions in the arylidene group gives rise to a new intense absorption band (460–500 m $\mu$ ). G.J.K.

**Spectrophotometric Study of Reversible and Non-reversible Transformations of Fe(III)-Phthalocyanine-tetrasulphonate in Aqueous Solution**

T. S. Glikman, M. E. Podlinskaya, and B. Ya. Dain

*Zhur. obshch. khim.*, **29** (June 1959) 1785–1793

Absorption spectra (325–800 m $\mu$ ) of aq. Fe(III)-phthalocyanine-tetrasulphonate (pH 2–10) have revealed the presence of a hydrolytic equilibrium—



the hydroxide complex undergoing slow decomposition with the formation of free OH radicals—



Visible light and absence of air promote the reduction. G.J.K.

**Monomethine Dyes—Derivatives of Pyrrocoline**

F. N. Stepanov and L. I. Lukashina

*Zhur. obshch. khim.*, **29** (Aug 1959) 2792–2795

Condensation of two molecules of pyrrocoline—



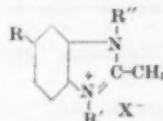
yields monomethine dyes of which there are two symmetrical forms (linking of 1,1' and 3,3'-positions by  $-CH-$ ) and one asymmetrical form (1,3'). These forms have been characterised spectrophotometrically (400–750 m $\mu$ ). G.J.K.

**Fluorine-containing Cyanine Dyes. VII—Synthesis of Cyanine Dyes from 6-Trifluoromethyl- and 6-Trifluoromethylsulphonylbenzimidazole**

L. M. Yagupol'skii and V. I. Troitskaya

*Zhur. obshch. khim.*, **29** (July 1959) 2409–2416

The synthesis of 2-methyl-3-phenyl-6-trifluoromethyl- and 2-methyl-3-ethyl-6-trifluoromethylsulphonylbenzimidazoles and of the corresponding quaternary salts (QS)



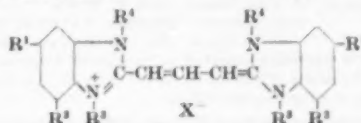
( $R = CF_3$ ,  $CF_3SO_2$ ;  $R' = C_6H_5$ ,  $C_6H_4$ ,  $\alpha$ - $C_{10}H_7$ ;  $R'' = CH_3$ ,  $C_2H_5$ ) is described. From QS eight symmetrical and two asymmetrical imidocarbocyanines and two rhodocyanines have been obtained. It is shown that the introduction of a trifluoro-methyl- and trifluoromethylsulphonyl group in position 6 of the benzimidazole nucleus causes hypsochromic shift of the absorption max. by 9 and 24 m $\mu$ , respectively compared with the unsubstituted 1,1', 3,3'-tetraethyl-imidocarbocyanine. G.J.K.

**Fluorine-containing Cyanine Dyes. VIII—Synthesis of Cyanine Dyes from 4,6-Bis(trifluoromethyl)-, 4-chloro-6-trifluoromethyl-, and 4-Chloro-6-trifluoromethylsulphonylbenzimidazole**

L. M. Yagupol'skii and V. I. Troitskaya

*Zhur. obshch. khim.*, **29** (Aug. 1959) 2730–2736

The synthesis of twelve tetrasubstituted imidocarbocyanines of formula—



( $R^1 = CF_3$ ,  $SO_2CF_3$ ;  $R^2 = CF_3$ ,  $Cl$ ,  $H$ ;  $R^3 = C_6H_5$ ,  $C_6H_4$ ,  $\alpha$ - $C_{10}H_7$ ;  $R^4 = CH_3$ ,  $C_2H_5$ ;  $X = I$  or  $ClO_4$ ), is described and their absorption spectra in alcohol given. G.J.K.

**Dyes derived from Benzothiocarbocyanine**

J. Swiderski, A. Roniewicz, and W. Markowski

*Roczniki Chem.*, **33** (1959) 735–8

*Chem. Abs.*, **54** (10 Jan 1960) 901

Preparation of 9-(*p*-iodophenyl)-, 9-(*p*-bromophenyl)- and 9-(*p*-chlorophenyl)- $N,N'$ -diethylbenzothiocarbocyanines is described. Introduction of Hal into the *p*-position had no effect on the position of the maximum of sensitisation. C.O.C.

**Thiobarbituric Acid-Methine Dyes**

H. Schmidt *Naturwissenschaften*, **46** (1959) 379–380

Heating oxidised fats with aqueous thiobarbituric acid yields a red dye,  $\epsilon_{max} = 532 m\mu$ . The same dye is obtained by treating the acid with malondialdehyde or its tetraethyl acetal, this identity was established by paper chromatography. It is formed from 2 mol. of thiobarbituric acid and 1 mol. malondialdehyde with elimination of 2 mol. water. Other dyes were prepared with vinylazones of malondialdehyde;  $HCOOH$  yields a yellow dye,  $\epsilon_{max} = 451-3 m\mu$ ; glutaric dialdehyde yields a blue dye having red fluorescence,  $\epsilon_{max} = 621-3 m\mu$ . C.O.C.

**Xanthylomethins**

R. Wizinger and V. Arni

*Chem. Ber.*, **92** (1959) 2309–2320

*Chem. Abs.*, **54** (25 Jan 1960) 1135

An account of the preparation from methylxanthylum perchlorate by classical methods of the symmetrical xanthocyanines up to the heptamethine. The properties of these dyes are given. C.O.C.

**Two New Naturally Occurring Anthocyanidins**

J. B. Harborne *Chem. and Ind.*, (27 Feb 1960) 229–230

Rosinidin, the principal pigment in the flowers of *Primula rosea* is shown to be 7,3'-dimethoxy-3,5,4'-trihydroxyflavylium and luteolinidin, occurring as a 5-monoglycoside with geranin in the bright scarlet petals of *Gerardia cardinalis*, has the constitution assigned by Lem and Robinson (*J.C.S.* (1931) 2732) to the synthetic product. C.O.C.



**The Blue Pigment of the Cornflower. I—Natural and Synthetic Anthocyanin Metal Complexes**

E. Bayer

*Chem. Ber.*, **91** (1958) 1115–1122*Chem. Abs.*, **53** (25 Nov 1959) 22289

The blue of cornflowers is produced by Fe and Al complexes of the anthocyanin. The petals have pH 3.8–5.8 and so the colour cannot be caused by an alkaline earth salt. Synthetic cyanin metal complexes were prepared and their spectra compared with those of the natural products. C.O.C.

**Mangiferin, the Colouring Matter of Mango (*Mangifera indica*)—III**

S. Iseda

*Kumamoto Joshidaigaku Gakujitsukiyo*, **9** (1957) 45–51

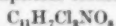
Mangiferin, obtained from mango bark, has the empirical constitution  $C_{18}H_{18}O_{11}$ . C.O.C.

**Pseudomonas Pigments**

R. Takeda

**III—Derivatives of Pyoluteorin***Bull. Agr. Chem. Soc. Japan*, **23** (1959) 126–130

Pyoluteorin, produced by a strain of *Pseudomonas aeruginosa*, has the empirical formula—

**IV—Structure of Pyoluteorin***Ibid.*, 165–171*J. Fermentation Technol.*, **37** (1959) 59*Chem. Abs.*, **54** (25 Jan 1960) 1488

Evidence shows this pigment has the constitution 2-(2,6-dihydroxybenzoyl)-X,X'-dichloropyrrole. C.O.C.

**Yellow Pteridine from the Bluish Green Alga *Anacystis nidulans***

H. S. Forrest, C. Van Baalen, and J. Myers

*Arch. Biochem. Biophys.*, **83** (1959) 508–520*Chem. Abs.*, **54** (25 Jan 1960) 1528

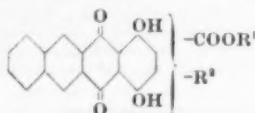
A yellow pteridine isolated in relatively large amounts from *A. nidulans* is shown to be 6,7-dihydro-2-amino-4,6-dihydroxy-6-propionylpteridine. C.O.C.

**Pyromycinones, a New Group of Red Actinomycin Pigments**

H. Brockmann, L. C. Plä, and W. Lenk

*Angew. Chem.*, **69** (1957) 477

A group of red pigments called pyromycinones has been isolated from mycelium and culture solutions of several *Streptomyces* stock. The main component is  $\eta$ -pyromycinone which is shown to have the structure—



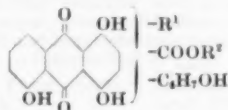
( $R^1 = CH_3$  when  $R^2 = C_4H_9$  and vice versa).

 **$\zeta$ -Pyromycinone**

H. Brockmann and W. Lenk

*Ibid.*, 477–8*Chem. Abs.*, **53** (25 Nov 1959) 21843

The above pigment has been isolated from the mixture of pyromycinones and shown to be—



The  $C_{17}H_{17}OH$  being so situated that distilling the pigment with Zn dust yielded a compound having an absorption spectrum characteristic of a naphthacene. C.O.C.

**Actinomycetes Dyes**

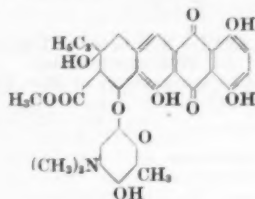
H. Brockmann and W. Lenk

**VI—Pyromycinones***Chem. Ber.*, **92** (1959) 1880–1903

Three crystalline dyes isolated from the *Streptomyces* strain DOA-1205 and designated  $\eta$ - (I),  $\zeta$ - (II) and  $\epsilon$ -pyromycinone are shown to be I—1,4,6-trihydroxy-8-carbomethoxy-9-ethylnaphthacenequinone, II—1,4,6,7-tetrahydroxy-8-carbomethoxy-9-ethyl-7,8,9,10-tetrahydronaphthacenequinone and III—the 9-OH derivative of II.

**VII—Pyromycin***Ibid.*, 1909–9*Chem. Abs.*, **54** (25 Jan 1960) 1468–1470

A red, antibiotically effective basic dye, pyromycin, was isolated as its HCl salt from *Streptomyces* strain DOA 1205. It has the constitution—



C.O.C.

**Specific Colour Reaction of Rutin (C.I. 75730) and Differentiation from its Analogues**

S. Kamiya

*Bunseki Kagaku*, **7** (1958) 717–8*Chem. Abs.*, **53** (25 Nov 1959) 22751

When 1 drop of a sample solution is mixed with a drop of water and 0.5 ml. of a solution of  $p$ - $NH_2C_6H_4OC_2H_5$  (0.1 mg./ml.) presence of rutin is shown by the mixture becoming green and then blue. Quercetin (C.I. 75670), 3'-4'-dihydroxyflavonol, morin (C.I. 75660), hesperetin, hesperidin, acacetin and acacetin 7-methylether do not give this colour reaction. C.O.C.

**Constitution of Vogetin—the Pigment from the Seeds of *Tephrosia vogelii***

S. Rangaswami and K. Hanumantha

*Proc. Indian Acad. Sci.*, **49A** (1959) 241–9*Chem. Abs.*, **54** (25 Jan 1960) 1509

Evidence to show that this yellow pigment is 5-methoxy-3,4',6,7-tetrahydroxyflavone. C.O.C.

**Fluorescent Material from the Skin of the Frog *Rana Nigromaculata*. I—Isolation and Properties of Rana-Chrom I**

T. Goto and T. Hama

*Proc. Japan Acad.*, **34** (1958) 724–9*Chem. Abs.*, **53** (25 Nov 1959) 22534

The yellow Rana-Chrom I which has strong blue fluorescence is shown to be 1-erythro-2-amino-4-hydroxy-6-(dihydroxypropyl)pteridine. C.O.C.

**Calcium Plumbate—a White to Blackish Brown Pigment**

V. Koutnik and J. Benes

*Chem. průmysl*, **9** (1959) 511–5*Chem. Abs.*, **54** (10 Jan 1960) 919

In making  $Ca_3PbO_4$  from PbO and Ca the two compounds were screened through a 60- $\mu$ -mesh sieve and dried; the mixture was again passed through the sieve and heated while stirring in an oxidising atmosphere in an electric oven. The optimum temperature was 750°C. Very slight excess of CaO gives best results. Impurities in the CaO affect the resulting pigment more than those in the PbO. Presence of up to 2%  $Fe_2O_3$  affects neither the process nor the product but  $SiO_2$  has an unfavourable influence. Steam and  $CO_2$  in the oxidising atmosphere cause the course of the reaction to be irregular and slow. Best results were obtained using pure PbO and conglutated  $CaCO_3$  as the raw materials at 800°C. in an O atmosphere. The amount of  $PbO_2$  rose to the maximum content value pf 60% during 2 hr. The product is white to blackish brown and has  $d$  5.6–5.7. C.O.C.

**Pigment, Cadmium Yellow (Cadmium Lithopone) Dry (C.I. Pigment Yellow 35)**

U.S. Federal Specification TT-P-342.

**Chrome Yellows (C.I. Pigment Yellow 34)**

A. J. Ryan and L. J. Williamson

**I—Chemistry of Manufacture***Paint J. Australia New Zealand*, **4** (2) (1959) 11–13

Reacting  $Pb(NO_3)_2$  with  $Na_2Cr_2O_7$  may result in crystals unsuitable as pigments. If basic Pb carbonate is present in correct amount to react with the  $HNO_3$  formed, a pigment results.  $Na_2CrO_4$  can replace  $Na_2Cr_2O_7$  if the pH is carefully controlled but may increase the cost. Basic Pb acetate is economical but the resulting pigment is not fast to light and the washing of the pigment requires great skill.  $Pb(OH)Cl$  reacted with  $Na_2Cr_2O_7$  and neutralised

with HCl yields a product suitable for the manufacture of chrome greens. Direct reaction of PbO with CrO<sub>3</sub> yields pigments of good fastness to light and tinctorial strength.

## II—Chemistry and Manufacture of Pale Chrome Yellows

*Ibid.*, (3) 9-11

These are produced by coprecipitation of PbCrO<sub>4</sub> and PbSO<sub>4</sub> from Pb(NO<sub>3</sub>)<sub>2</sub> with Na<sub>2</sub>CrO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. The proportions needed vary primrose yellows containing up to 40% sulphate and lemon yellows 30%. In some cases part of the PbSO<sub>4</sub> is coprecipitated and the remainder precipitated separately. Stirring can cause crystal growth, resulting in a homogeneous product by adsorption.

C.O.C.

## Chrome Yellows (C.I. Pigment Yellow 34)—Chemistry of Manufacture—III

A. J. Ryan and L. J. Williamson

*Paint J. Australia and New Zealand*, 4 (5) (1959) 11-13  
*Chem. Abs.*, 54 (25 Jan 1960) 1891

The degree to which lead chromate crystals will be rhombic or monoclinic, their size, stability and other technological properties is dependent on the materials used, the pH of solutions and the rate at which ion-exchange reactions during and after precipitation modify the original particle size and shape. This ageing process may occur too quickly if solubility is too great.

C.O.C.

## PATENTS

### Oxidation Bases

FBY

BP 818,110

N-Glycosides, especially N-glucosides of aromatic amines or their reduction products, e.g. 1-arylamino-1-deoxyglycitol, used as oxidation bases on organic fibres yield browns to blacks. They are stable in dye liquors or printing pastes at normal temperatures but split into oxidisable amines and sugars when heated. The sugars act both as protective colloids for the fibre and, because they slow down the oxidation, as penetrating agents. If oxidation is slowed down too much then it can be overcome by use of a strong catalyst, e.g. K ferrocyanide or phloroglucinol. Thus cotton cloth is printed with a paste made up of water (19 parts by vol.), 2% ammonia (5), polyglycoether mol.wt. 200 (3 parts by wt.), thiodiglycol (2), tragacanth 65/1000 (50), NH<sub>4</sub>Cl (5), NaClO<sub>2</sub> (4) and NH<sub>4</sub> vanadate 1:100 (2), steamed for 10 min., boiled and soaped. This yields a strong black print. The same result is obtained on rayon, acetate, nylon, polyester, polyurethane or acrylic fibres.

A.T.P.

## Coupling Components for use in Diazotype Compositions to produce Yellows Highly Opaque to Ultraviolet Radiation and Visually Dense Sepias

General Aniline

BP 828,390

A mixture of a monohydric phenol capable of yielding a yellow dye having high absorption for ultraviolet radiation, e.g. o-hydroxyphenylurea, and 1-hydroxy-3-sulphamyl naphthalene to form the sepia.

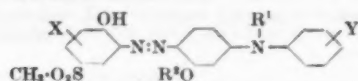
C.O.C.

## Metallisable Monoazo Disperse Dyes having a Diphenylamine Residue

Eastman Kodak Co.

USP 2,887,477

The title dyes of formula—



(X = H, NO<sub>2</sub>, or Cl; Y = H, CH<sub>3</sub>, OCH<sub>3</sub>, or Cl; R¹ = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, or C<sub>2</sub>H<sub>5</sub>CN; R² = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or C<sub>2</sub>H<sub>5</sub>OH) may be metallised on the fibre, e.g. cellulose acetate, especially with Ni(SCN)<sub>2</sub>, or in substance, when pigments suitable for colouring spinning dopes are formed. Thus diazotised 2-amino-4-methylsulphonylphenol is coupled in a propionic/acetic acid mixture with 3-chloro-3'-hydroxydiphenylamine giving the monoazo compound (X, R¹, and R² = H; Y = 3-Cl) which dyes cellulose acetate orange, converted to red by padding with aq. Ni(SCN)<sub>2</sub> and steaming at 100°C. for 10 min.

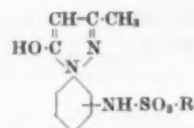
E.S.

## Metal(Chromium and Cobalt)-complex Monoazo Pyrazolone Dyes for Wool, etc.

FBY

BP 819,174

Pyrazolone derivatives—



(R = Alk or phenyl), prepared e.g. by condensing alkyl- or aryl-sulphonic acid chlorides with 1-aminophenyl-3-methyl-5-pyrazolones, are coupled with diazotised o-aminophenols or anthranilic acids, free from SO<sub>3</sub>H and non-complexing COOH groups, to give monoazo compounds whose 1:2-complexes with Co and Cr dye wool, nylon, etc. from neutral or weakly acid baths. Thus diazotised 2-aminophenol-4-sulphonamide is coupled with 1-(m-benzenesulphonylaminophenyl)-3-methyl-5-pyrazolone, and the product, dissolved in hot aq. NaOH, is heated at 95-100°C. with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and glucose to give the Cr-complex which dyes wool orange.

E.S.

## Metallisable and Metal-complex Monoazo Pyrazolone Dyes for Wool, etc.

Gy

BP 819,314

1-Phenylmethyl(or phenylethyl)-3-methyl-5-pyrazolone couples with suitable diazotised o-aminophenols or anthranilic acids to give monoazo compounds which may be metallised in substance or on the fibre. These pyrazolone compounds are prepared e.g. by condensing benzaldehyde, phenylacetaldehyde or acetophenone with an alkyl hydrazineformate to give acylhydrazones which are hydrogenated to form acylhydrazines. Hydrolysis of the acyl group then gives the hydrazines, which are condensed with e.g. ethyl acetoacetate to give the pyrazolones. Diazotised anthranilic acid couples with 1-(α-phenylethyl)-3-methyl-5-pyrazolone to give a yellow applicable to wool by the metachrome process. The metal-complex of 2 mol. of this dye with 1 atom of Cr dyes wool yellow from a neutral or weakly acid bath.

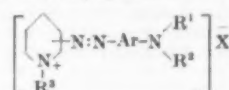
E.S.

## Basic Monoazo Dyes for Polyacrylonitriles

American Cyanamid Co.

USP 2,893,816

Quaternised heterocyclic monoazo dyes give deep colours on polyacrylonitrile fibres. Particularly suitable are the pyridinium compounds—



(the azo group is in the 2 or 4 position of the pyridine nucleus; Ar = benzene or naphthalene series radical, the amino N atom being attached to a position conjugated with the azo group, i.e. o- or p- in the same ring, or also 5- or 7-position in a naphthalene residue; R¹ = Alk, cycloalkyl, Ar, aralkyl, or alkenyl; X = an anion; R², R³ = H, Alk, acyl, alkenyl, cyclic alkyl, or together with the N atom may form a heterocyclic ring). Thus 2-aminopyridine is boiled with KOH in xylene in an atmosphere of nitrogen, and p-nitroso-N,N-dimethylaniline is then added and boiling continued. The monoazo compound so produced is boiled in toluene with dimethyl sulphate to give the violet basic dye (Ar = p-C<sub>6</sub>H<sub>4</sub>; R¹, R², R³ = CH<sub>3</sub>; X = CH<sub>3</sub>SO<sub>3</sub>).

E.S.

## Reactive Dyes for Cellulosic Fibres

CFM

BP 827,570

Water-soluble dyes containing at least one SO<sub>3</sub>F group when applied to cellulose, either by impregnation with an aqueous solution or printed on as a paste, and then steamed acylate the fibre, HF being split off. It is preferable that acid-binding agents be present. Thus cotton impregnated with an aqueous solution of the dye 1-aminobenzene-3-sulphofluoride hydrochloride-1-(4'-sulphonyl)-5-pyrazolone-3-carboxylic acid and then steamed in presence of Na acetate is dyed a greenish yellow fast to wet processing, very good fastness to light and dischargeable to a pure white. A list of 34 similar dyes is given.

C.O.C.

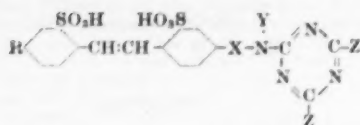
## Stilbene Azo Compounds having a Cyanuric Residue—Reactive Dyes for Cellulose

ICI

BP 828,353

The stilbene azo compounds—

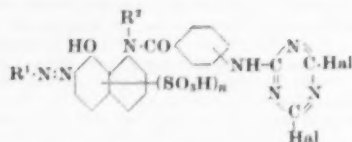




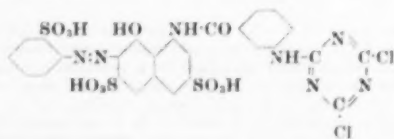
(R = Hal, NO<sub>2</sub>, subst. amino other than AlkNH, acylamino, a 1',2',4,5-naphthatriazolyl group which may be substituted by SO<sub>3</sub>H, a 4-aryloxy-3-subst.-pyrazo-5-on-1-yl group wherein the aryloxy may be subst. other than with NH<sub>2</sub>, NHalk, or a metallisable system, or a group -N=N-B where B = radical of coupling component; X = direct link or a divalent aryloxy group which may be subst. other than with NH<sub>2</sub>, NHalk, or a metallisable system; Y = Hal or Alk; Z = Hal; at least one of the groups R and X contain at least one azo group) are mainly yellow reactive dyes, particularly for cellulose. Thus the aminomonoazo compound obtained by coupling diazotised 4-amino-4'-nitrostilbene-2,2'-disulphonic acid with sodium aniline-methane sulphonate and subsequently hydrolysing with dilute alkali is condensed with 1 mol. of cyanuric chloride to give a yellow dye (R = NO<sub>2</sub>; X = 4'-phenylazo; Y = H; Z = Cl) fast to washing when applied to cellulose in conjunction with an alkaline aftertreatment. E.S.

#### Red Reactive Monoazo Dyes for Cellulose

ICI BP 829,042



(R<sup>1</sup> = Ar free from OH, NH, or NHalk groups; n = 1 or 2; the NH group is in the *m*- or *p*-position to the CO group in the benzene ring; R<sup>2</sup> = H or Alk of < 7 C) are reactive dyes for cellulose, faster to storage in moist, acid conditions than the similar dyes of BP 785,222 (J.S.D.C., 74 (1958) 58) in which the triazine ring is directly attached to the N of the naphthalene nucleus. Thus *N*-*m*-aminobenzoyl-H acid is condensed with a suspension in aq. acetone of cyanuric chloride. Diazotised orthanilic acid is then added giving—

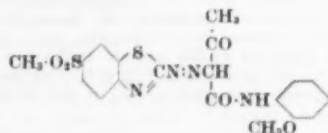


applied to cotton by padding followed by steaming in presence of NaOH. E.S.

#### Metallisable Monoazo Disperse Dyes from 2-Aminobenzthiazoles

Eastman Kodak Co. BP 827,655

Diazotised 2-aminobenzthiazole derivatives are coupled with suitable keto-enol compounds to give disperse dyes which may be metallised on the fibre. Or the metal-complexes prepared in substance may be applied to e.g. nylon or polyacrylonitrile fibres, or incorporated in the spinning solutions of thermoplastic fibres. Thus diazotised 2-amino-6-methylsulphonylbenzthiazole is coupled with acetacet-*o*-aniside giving—



which dyes cellulose acetate pale yellow, converted to stronger lemon-yellow by padding with aq. Ni(SCN)<sub>2</sub>, drying, and steaming at 5 lb./sq.in. for 20 min. E.S.

#### Metal(Chromium and Cobalt)-complex Monoazo Dyes for Nylon

General Aniline BP 829,125

The complexes containing 1 atom of Co or Cr to 1 mol. of the monoazo compound 2-aminophenol-4-sulphonamide-3-methyl-1-phenyl-5-pyrazolone dye nylon from a neutral bath. The Cr-complex is a yellowish-orange. E.S.

#### Aminoazo Compounds—Rearrangement of Diazo-amino Compounds in Presence of a Friedel-Crafts Catalyst

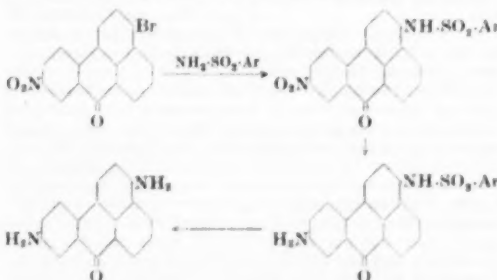
The B.F. Goodrich Co. USP 2,894,942

The rearrangement of diazoamino compounds to give aminoazo compounds is facilitated by the presence of e.g. AlCl<sub>3</sub>, BF<sub>3</sub>, benzotrifluoride, etc. Thus to a mixture of aniline (750 g.) and conc. HCl (83 g.) is added a solution of NaNO<sub>2</sub> (50 g.) in water (150 ml.) at 20–31°C. After 15 min. vigorous stirring water is separated from the organic layer, and the latter is neutralised with Na<sub>2</sub>CO<sub>3</sub> (15 g.). AlCl<sub>3</sub> (22.75 g.) is then added and a yield of 85–4% of *p*-aminoazobenzene, based on the NaNO<sub>2</sub> used, is obtained after ca. 140 min. at 55°C. E.S.

#### 3,9-Diaminobenzanthrone—Intermediate for Disazo Dyes

American Cyanamid Co. USP 2,891,048

3-Bromo-9-nitrobenzanthrone, obtained from benzanthrone by bromination followed by nitration, gives the 3,9-diamino compound by the reactions—

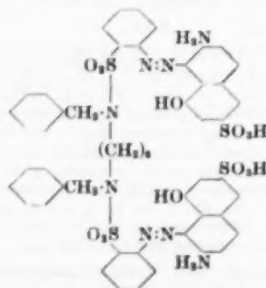


(Ar = e.g. *p*-tolyl). It may be tetrazotised and coupled with aminonaphthol-sulphonic acids to give direct dyes, deeper in hue than the corresponding dyes from tetrazotised benzidine; e.g. H acid gives a green-blue. The tetrazo compound may also be used to produce azoic dyeings, e.g. on cotton impregnated with 3-hydroxy-2-naphtho-*a*-naphthylamide it gives a blue. E.S.

#### Orange and Red Disazo Acid Dyes

Gy BP 828,698

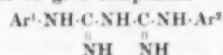
Diphenols, aminophenols, dinaphthols, or diamines, and particularly secondary diamines, are condensed with 2 mol. of *o*-nitrobenzenesulphonyl chloride, the nitro groups are reduced, and the resulting diamines are tetrazotised and coupled with β-naphthylaminesulphonic acids to give the title dyes. Thus bis(*o*-aminobenzene-sulphonyl)-*N,N'*-dibenzyl-1,6-hexamethylenediamine is tetrazotised with nitrosyl sulphuric acid, and coupled in presence of acetic acid with 2 mol. of γ acid, giving—



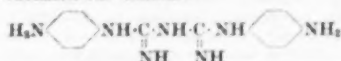
which dyes wool bright yellowish red from a neutral or weakly acid bath. E.S.

**Disazo Dyes having a Biguanide Residue**American Cyanamid Co. *USP* 2,889,317

Primary arylamines in the form of their hydrochlorides react readily with the sodium salt of dicyanamide on boiling in water to give compounds—



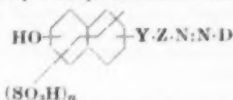
The reaction proceeds not only with simple amines such as *m*-aminophenol but also with *J* acid and certain aminoazo compounds, so that symmetrical and unsymmetrical disazo dyes can be readily made, in substance or on the fibre, e.g. cellulose. Thus by condensing 2 mol. of *p*-aminocetanilide with 1 mol. of sodium dicyanamide, followed by hydrolysis of the acetyl groups there is obtained the diamine—



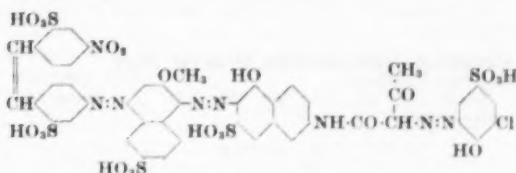
which may be tetrazotised and coupled with 2 mol. of *J* acid to give a red direct dye. Or the tetrazo solution may be used as an azoic diazo component. *E.S.*

**Copperable Trisazo Direct Dyes**Gy. *BP* 828,826

The diazo compound of a *p*-aminoazo compound having an  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ , or  $\text{OCH}_2\text{-COOH}$  group in the *o*-position to the diazo group is coupled with a monoazo compound—



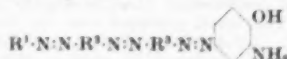
(coupling takes place *ortho* to the naphtholic OH;  $n = 0, 1, \text{ or } 2$ ; Y = direct link or  $\text{-NH-CO-(NH)}_m\text{-Ph-}$ , where  $m = 0 \text{ or } 1$  and Ph = *m*- or *p*-phenylene; Z = acylacet-amido radical or a 5-pyrazolone radical; D = residue of a diazo component of benzene or naphthalene series providing a metallisable group in *o*-position to the azo link). The products dye cellulose grey, olive, or green, and may be aftercoupled on the fibre; those having 2  $\text{SO}_3\text{H}$  groups may be coppered in substance to give complexes of sufficient solubility. Thus diazotised 4-amino-4'-nitrostilbene-2,2'-disulphonic acid is coupled with 2-methoxy-1-naphthylamine-6-sulphonic acid, and the product is diazotised and coupled with the monoazo compound, 2-amino-6-chlorophenol-4-sulphonic acid-*N*-aceto-acetyl-*J* acid, to give—



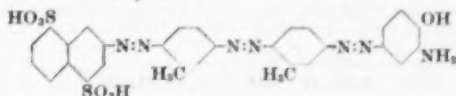
Stirring at 95–100°C. with aq.  $\text{CuSO}_4$  gives the copper complex which dyes cellulose olive green of good fastness to anti-crease processing. *E.S.*

**Metal(Copper and Nickel)-complex Tetrakisazo Direct Dyes**S *BP* 828,668

Aminotrisazo compounds—



( $\text{R}^1 = \text{aryl}$  preferably of the naphthalene series containing 2  $\text{SO}_3\text{H}$  groups;  $\text{R}^2, \text{R}^3 = \text{aryl}$  groups preferably of the benzene series), or their *O*-alkylated or *O*-acylated derivatives, are diazotised and coupled with *o*-coupling naphthols and the products metallised (after removing the acyl groups if present) to give the title dyes. Thus the aminotrisazo compound—



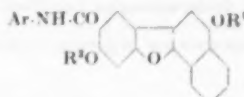
is diazotised and coupled in presence of pyridine with 2-naphthol-4-sulphonic acid. Stirring with aq.  $\text{CuSO}_4$  at 70°C. gives the copper-complex of the tetrakisazo compound, which dyes cotton brown. *E.S.*

**Diazotising Primary Arylamines by means of a Boron Trifluoride/Nitrous Anhydride Complex**Purdue Research Foundation *USP* 2,894,941

Nitrogen peroxide dissolved in e.g. nitroethane is cooled to  $-70^\circ\text{C}$ . and nitric oxide is passed in to give nitrous anhydride ( $\text{N}_2\text{O}_3$ ). Gaseous  $\text{BF}_3$  is then bubbled into the solution, giving the complex  $\text{BF}_3\text{-N}_2\text{O}_3$ , which reacts at 0–50°C. in organic solvents with even such weakly basic amines as 2,4-dinitroaniline to give the diazonium compounds in a dry, stable form. *E.S.*

**Benzonaphthofuranol Derivatives—Azoic Dye Coupling Components**American Cyanamid Co. *USP* 2,893,986

Derivatives of benzonaphthofuranol, particularly the carboxyarylates—



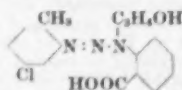
( $\text{R}^1, \text{R}^2 = \text{H}$ , lower Alk, or acyl), are coupling components for azoic dyes, giving deep shades, e.g. browns. Thus naphthoquinone is condensed with 1 mol. of resorcinol in acetic acid containing a little  $\text{H}_2\text{SO}_4$ . After purifying by acetylation, crystallisation of the acetyl compound, and hydrolysis, the dihydroxy compound is monomethylated. Treatment with  $\text{CO}_2$  under pressure then introduces the  $\text{COOH}$  group, converted into the *p*-chloroanilide ( $\text{Ar} = \text{p-chlorophenyl}$ ;  $\text{R}^1 = \text{CH}_3$ ;  $\text{R}^2 = \text{H}$ ) by refluxing in toluene with *p*-chloroaniline and  $\text{PCl}_5$ . It is padded on cotton and developed with e.g. diazotised 2-methoxy-4-nitroaniline, which gives an olive. *E.S.*

**Stable Diazotisable Amine/Nitrite Compositions for Production of Azoic Dyes**L. N. Stanley and F. W. Posselt *USP* 2,893,815

A mixture of primary arylamine devoid of solubilising groups, an organic nitrite (optionally mixed with an alkali-metal nitrite) a non-ionic and a cationic surface-active agent, and a water-miscible solvent, has good stability and gives a clear diazo solution on acidifying with e.g. aq.  $\text{HCl}$ , which can thus be used to develop an azoic dyeing on a fibre impregnated with a suitable coupling component. Thus, 2-amino-5-chlorotoluene (18.2 g.), a non-ionic castor oil/ethylene oxide condensate (10 g.), glycol monoethyl ether (13 g.), and diethylene glycol (18.2 g.) are stirred together, and a solution of diisopropylamine nitrite (20.7 g.) in water (10 g.) containing a long-chain alkyl dimethylbenzyl ammonium chloride (9 g. of 50% aq. soln.) is added, and the mixture diluted with water (to 100 cc.). *E.S.*

**Triazenes Suitable for Production of Azoic Prints by Neutral Steaming**Pharma-Chemical Corp. *USP* 2,897,186

Diazo compounds from amines devoid of solubilising groups condense with *N*-alkyl- or *N*-(hydroxyalkyl)-anthranilic or -orphanilic acids to give triazenes which regenerate the diazo compound readily, and can thus be used in conjunction with conventional coupling components to yield azoic prints on steaming under neutral conditions. Thus *o*-chlorobenzoic acid condensed with ethanolamine in presence of a Cu catalyst gives *N*-β-hydroxyethylanthranilic acid, which condenses with diazotised 2-amino-4-chlorotoluene under alkaline conditions giving the triazene—



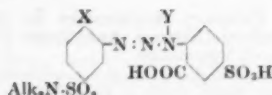
This is mixed with a thickened alkaline solution of 3-hydroxy-2-naphtho-*o*-toluidide, printed on cotton, dried, and steamed at 95–100°C. to give bright red. *E.S.*

### Triazines for Azoic Prints which Develop under Neutral Conditions

Ciba

BP 829,570

The triazines—



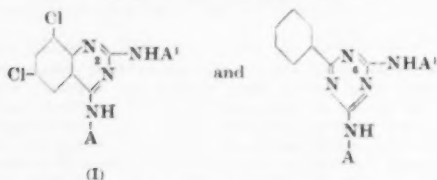
(X = CH<sub>3</sub>, OCH<sub>3</sub>, or OC<sub>2</sub>H<sub>5</sub>; Y = isopropyl or isobutyl) when mixed with azoic coupling components, thickeners, and alkali, printed and dried, give the azoic dye on neutral steaming without a halogeno-fatty acid salt being present. Thus the triazine from diazotised 2-aminotoluene-4-sulphonediethylamide condensed with *N*-isopropyl-5-sulphoanthranilic acid (X = CH<sub>3</sub>; Y = isopropyl; Alk = C<sub>2</sub>H<sub>5</sub>) mixed with 3-hydroxy-2-naphtho-2',5'-dimethoxy-4'-chloroanilide gives a yellowish-red when steamed 5–8 min. at 100°C. under neutral conditions. E.S.

### Homogeneous Anthraquinone Vat Dyes

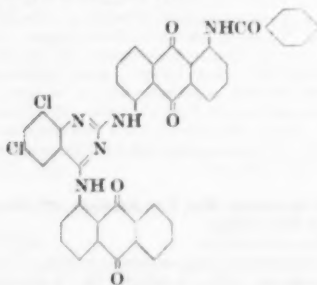
BASF

BP 829,699

The title compounds are of general formula—



(A and A' = radicals of two different vat-dyeable amines of the anthraquinone series). They are obtained by condensing the corresponding quinazolines or triazines (containing Cl in positions 2 and 6 respectively) with vat-dyeable anthraquinone-amino compounds. Thus, 2,4,6,8-tetrachloroquinazoline (133) is added at 100°C. to 1-aminoanthraquinone (112) in *N*-methylpyrrolidone (700). Reaction at 110°C. for 1 hr. and cooling gives the intermediate product II (201) of I where A is an anthraquinone radical and position 2 is still substituted by Cl. II (45) is then condensed with, e.g. 1-amino-5-benzamidoanthraquinone (34) in nitrobenzene (660) at 190°C. for 3 hr. Filtration at 100°C. followed by a methanol wash gives the yellowish red vat dye—



Previously known compounds related to the above were mixtures of structures substituted AA, and A'A' in addition to AA'. These suffered from many disadvantages, e.g. unattractive hue and unequal exhaustion rates, which the present compounds do not. A.T.P.

### Anthraquinone Vat Dyes

Ciba

BP 829,527

Grey vat dyes of good fastness and levelling power are obtained by carbolising (preferably with AlCl<sub>3</sub> in pyridine at 120–125°C.) an oxidation product of a 1-aminoanthraquinone containing an H atom in the 4-position. The products may be acylated or reacted with a compound containing exchangeable halogen after the oxidation and before the carbolisation. The dyes are thus similar to those of BP 794,849 (J.S.D.C., 74 (1958) 602), in which MnO<sub>2</sub>, CrO<sub>3</sub> or an alkali metal bichromate in aq. H<sub>2</sub>SO<sub>4</sub> is used as oxidising agent in the first stage. The present

method has advantages in that oxidation is carried out with an alkali metal salt of a chloric acid or of a persulphuric acid in aq. H<sub>2</sub>SO<sub>4</sub>. Thus, 1-aminoanthraquinone (55.8) is stirred into 80% H<sub>2</sub>SO<sub>4</sub> (390) and the mass diluted with 25% H<sub>2</sub>SO<sub>4</sub> (240) and ice (250). At 20°C., K persulphate (97.8) is added over 5 hr. and the whole stirred for 15 hr. The black reaction product (48.7) (I) is isolated by filtration and washed with H<sub>2</sub>O and MeOH. Finely-ground I (5) is added to a melt of AlCl<sub>3</sub> (50) in pyridine (60), the melt stirred for 17 hr. at 170–175°C. and poured on to 4% NaOH (2000). The resulting grey vat dye is precipitated by adding sodium *m*-nitrobenzene sulphonate. A.T.P.

### Copper Phthalocyanine (C.I. 74160)

General Aniline

BP 819,457

Cu phthalocyanine of high quality is produced, without any lengthy purification process, by heating at 200°C. phthalic anhydride, a Cu salt and urea in presence of a molybdate catalyst and a water immiscible inert organic solvent. Water at 50–85°C. is mixed with the reaction mass which has been cooled to < 120°C. (preferably to 140–150°C.). The ratio of water to reaction mass must be at least 4:1. The product is best isolated by filtration of the aqueous mass and solvent is recovered from the aqueous layer. Thus, phthalic anhydride (300 parts by wt.), cupric chloride (70), urea (600), NH<sub>4</sub> molybdate (2) and trichlorobenzene (1500) are refluxed at 200°C. until reaction is complete. The mass (1 part by vol.) is cooled to 140°C. and fed slowly into a hammermill with water (4) at 50°C. The aqueous layer is agitated and filtered, the cake steam stripped and trichlorobenzene recovered from the aqueous filtrates. A.T.P.

### Stable Emulsions of Indocarbon Sulphur Dyes

General Aniline

USP 2,893,813

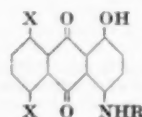
Stable, ready to use aqueous emulsions of sulphur dyes contain an indophenol sulphur dye of *p*-hydroxyphenyl β-naphthylamine in reduced form (I) (20–30 parts by wt.), an aliphatic hydroxy compound of 1–10 C atoms (5–15), e.g. butanol, ethylene glycol monoalkyl ether, ethylene glycol, an ionic or non-ionic surface active agent (5–20), and Na<sub>2</sub>S (2–10). (I) are prepared *in situ* at pH 10–12.5 without use of sodium hydrosulphite, thus saving time and expense compared with earlier methods. Thus, 4-hydroxy-2-naphthylamine (45), water (40), ethylene glycol monoethyl ether (40), NaOH (5), Na<sub>2</sub>S (10), 8 (75) and a formaldehyde-sodium naphthalene sulphonate condensate (10) are refluxed for 36 hr. Cooling to room temperature and dilution with half its weight of 10% aq. NaOH gives a stable emulsion of pH 11.0, from which cotton is dyed deep black. A.T.P.

### Metallised Anthraquinone Disperse Dyes

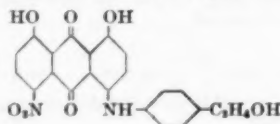
Eastman Kodak Co.

USP 2,895,967

Metal (Cr, Co, Cu, Fe, Mn, Ni, V) containing compounds—



where R is a benzene residue, one X is -OH and the other X is -NO<sub>2</sub>, are blue dyes for synthetic fibres and the coloration of spinning dopes. They are faster to light, washing, and sublimation than analogous unmetallised structures. The metal complex may be formed before dyeing, e.g. 1,8-dihydroxy-5-nitro-4-*p*-toluidinoanthraquinone (1.95) is refluxed in acetone (30). 28% aq. NH<sub>4</sub>OH is added, followed by nickelous acetate (1.37) in hot 50% aq. acetone (30); the mixture is refluxed for 150 min. and drowned into water to give the dark blue metal complex. Alternatively, the metal complex may be formed on the fibre, e.g. cellulose acetate dyed with 2% of—



is padded with a 2% aq. Co thiocyanate to 60–100% pick-up. The fabric is dried at room temperature, aged at 5 p.s.i. for 20–30 min. and scoured at 60°C. It is slightly greener than the original and very fast to washing.

A.T.P.

### $\alpha$ -Hydroxy- $\beta$ -nitroanthraquinones

ICI BP 827,563

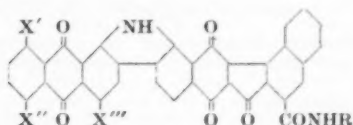
An anthraquinone having Hal, OH or NO<sub>2</sub> in an  $\alpha$ -position is treated with nitrite and acid in a water-miscible solvent, giving an  $\alpha$ -hydroxy- $\beta$ -nitroanthraquinone in good yield, e.g. 1-hydroxyanthraquinone (2 parts), sodium nitrite (4) and dimethylformamide (80) are stirred at 150°C. for 6 hr. Benzoic acid (3.3) in dimethylformamide (80) is then gradually added over 18 hr. at 150°C. After a further 6 hr. at 150°C. the mixture is poured into 5% aqueous hydrochloric acid (400). The yellow precipitate of 1-hydroxy-2-nitroanthraquinone is filtered off, washed with water and dried.

P.B.S.

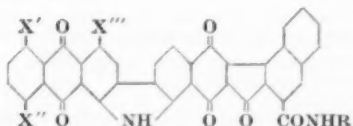
### Anthraquinone Vat Dyes

DuP USP 2,893,998

Fast to light reddish brown vat dyes of good build-up are anthraquinone-carbazole-dinaphthalenone compounds (I)—



and



(two of X = H, the other H or a monocyclic aroylamino radical, e.g. benzoylamino; R = radical of an aromatic compound of < 11 C and which is free of water-solubilising groups). Thus 2,3-dichloro-5-nitro-1,4-naphthoquinone (1-3) is condensed with 3-hydroxy-2-naphthylamide (1-3) in pyridine (15) at 100–110°C. for 3–4 hr., stirred cold for 12 hr. and filtered. Hot water extraction of the residue gives a mixture of 9- and 12-nitro-8,13-dioxodinephthol [2,1:2',3']-furan-6-carboxanilide (1-8) (II). This (9) is reduced at 35–40°C. for 75 min. with 30% NaOH (90) and hydros (27) in water (200). Air oxidation gives the amino analogue (III) of (II). This (8-6) is condensed with 1-benzamido-4-chloroanthraquinone (7-2) at 185–190°C. for 10 hr. in presence of Na<sub>2</sub>CO<sub>3</sub> (4), Cu acetate (0-2), and nitrobenzene (65). The resulting anthrimide (10) is cyclised at 55–60°C. for 30 min. with AlCl<sub>3</sub> (40) in nitrobenzene (120) to give (I) where R = phenyl, X' and X'' = H, and X''' = benzamido. The dye is believed to be a mixture of the *cis* and *trans* isomers of structure (I).

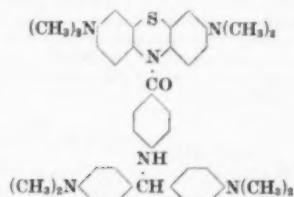
A.T.P.

### 10-(4-N-Leucauraminebenzoyl)-3,7-bis-(dimethylamino)-phenothiazine

Caribonum

BP 817,564

The title compound of formula—



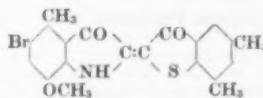
is colourless but when subjected to slightly acidic oxidising conditions is converted to a blue compound of good fastness to light. It is prepared by condensing Michler's hydrol with 10-(4-aminobenzoyl)-3,7-bis-(dimethylamino)-phenothiazine and is used in transfer sheet material. C.O.C.

### Indigoid Vat Dye

FH

BP 828,704

The dye—



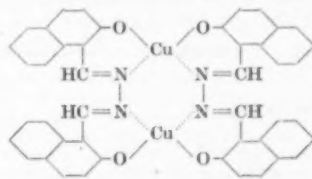
is a more greenish blue and faster to light than the corresponding Cl containing dye made by the process of GP 546,006. The present dye is made by condensing 4-methyl-5-bromo-7-methoxyisatin- $\alpha$ -chloride with 5,7-dimethyl-3-hydroxyl-1-thionaphthene. C.O.C.

### Azine—Heavy Metal Complex Pigments

American Cyanamid Co.

USP 2,877,252

Heavy metal chelates of hydroxyarylazines (I) are obtained by heating (I) with a metal salt of a fatty acid (metal of atomic number 24–30) in presence of a *N*-alkylamide of a fatty acid. The pigments thus obtained have in many cases particle size enabling them to be used without any further treatment. Especially useful (I) are the azines derived from 2-hydroxy-1-naphthaldehyde. Thus, an outstanding chocolate-brown pigment is—



obtained by adding 2-hydroxy-1-naphthaldehyde (10-2) to a solution of formyldimethylamine (474) and cupric acetate monohydrate at 110–115°C. The copper chelate separates on cooling and has outstanding fastness to solvent bleeding (xylol and butanol) and very good light fastness. A.T.P.

### Tetrazaporphin Derivatives having Aromatic Substituents containing Sulphonic Acid Groups and Primary Amino Groups

BASF

BP 827,568

A tetrazaporphin sulphonic acid chloride is condensed with an arylsulphonic acid, containing at least two primary amino groups, such that one mol. diaminoarylsulphonic acid forms one mol. of hydrogen chloride and using less of the diaminoarylsulphonic acid than is equivalent to the sulphonic acid chloride groups. The unreacted sulphonic acid chloride is then either—(a) saponified to sulphonic acid groups, (b) reacted with ammonia or a primary or secondary aliphatic monoamine, giving products of slight water solubility which are cotton dyes, (c) reacted with monoaminoalkyl- or -arylsulphonic acid, giving products of good water solubility and practically no affinity for cellulose. The products of (b) or (c) may also be obtained by reacting the tetrazaporphin sulphonic acid chloride with a mixture of the diaminoarylsulphonic acid and the other amine designated in (b) or (c). They are intermediates for dyes.

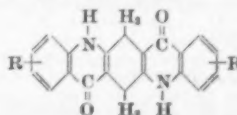
P.B.S.

### Dihydro-quinacridones

DuP

BP 828,051

Intermediates, especially for pigments of formula—



(R = H, Hal, Alk or alkoxy of 1–4 C) are made by adding a dialkyl succinate to a dispersion of a sodium alkoxide in a high boiling solvent (b.p. 240–300°C.), heating to form a dialkyl succinyl succinate, neutralising the mixture, forming a dialkyl-2,5-diarylamino-3,6-dihydroterephthalate by heating the dialkyl succinyl succinate *in situ* with excess of an arylamine in presence of a dissolved acidic catalyst while removing the water of condensation under reduced pressure, again neutralising the mixture,



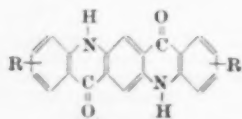
distilling off excess arylamine, introducing an inert gas, and heating the solution in absence of oxygen to 240–300°C. for 0.75–3.0 hr. P.B.S.

### Linear Quinacridone Pigments

DuP

BP 828,052

Pigments of formula—



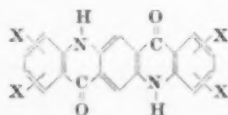
(R = H, Hal, Alk or alkoxy of 1–4 C) are prepared by oxidising 6,13-dihydroquinacridones (prepared by the method of BP 828,051, see preceding abstract) with heating in presence of an alkaline alcoholic medium containing nitrobenzene-*m*-sodium sulphonate or sodium polysulphide. They can be produced in three crystal phases and the X-ray patterns of these are given. Details of milling and the effect of solvents on the crystal phases during milling are given. The products are red to violet pigments of good tinctorial strength, light fastness, and outdoor durability. P.B.S.

### Symmetrical Tetrahalogen Substituted Quinacridones

DuP

BP 828,053

Pigments of formula—



(X = Hal) are prepared by a process similar to that described in BP 828,051 and 828,052 (see preceding abstracts) but using as the arylamine a dihalogenoaniline. The products are brilliant orange to yellowish-red pigments of high fastness to light, solvents and chemicals. P.B.S.

### Tetrazaporphin Derivatives Containing Methylene-arylsulphonic Acid Groups

BASF

BP 827,569

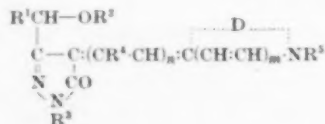
A halogenmethyltetrazaporphin is reacted at ca. 100°C. with a hydroxy- or mercapto- and/or aminohydroxyaryl compound (in which the substituents may be alkylated or acylated and which may contain other substituents) in aqueous sulphuric acid (sp. gr. > 1.6) or in anhydrous sulphuric acid and/or chlorosulphonic acid. The time of heating is varied according to the degree of sulphonation required. After cooling, the melt is poured into water, the precipitate filtered off, neutralised, and dried. The products are soluble in water and are weak blue-green dyes for cotton, wool, and nylon. P.B.S.

### Cyanine Dyes

Ilford

BP 828,847

Dyes of formula—



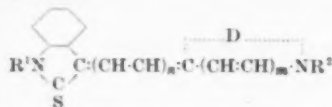
(R<sup>1</sup> = H or Ar; R<sup>2</sup> = H or carboxylic acyl or aryl sulphonyl; R<sup>3</sup> = subst. or unsubst. Ar; R<sup>4</sup> = H or Alk; R<sup>5</sup> = Alk, hydroxyalkyl or Ar; n and m = 0 or 1; D = atoms to complete a 5- or 6-membered nucleus), e.g. the red 4'-1',3',3'-trimethyl-2'-indolinylidene-ethylidene-3-hydroxymethyl-1-phenyl-5-pyrazolone, and their manufacture are described. They are also used as intermediates to make other cyanine dyes. Thus the above dye when heated with acetic anhydride yields the red 3-acetoxy-methyl-4'-1',3',3'-trimethyl-2'-indolinylidene-ethylidene-1-phenyl-5-pyrazolone. C.O.C.

### Polymethine Dyes

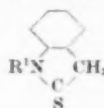
Ilford

BP 829,584

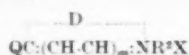
Dyes of formula—



(R<sup>1</sup> = Alk, Ar or aralkyl; R<sup>2</sup> = Alk, hydroxyalkyl or Ar; D = atoms to complete a 5- or 6-membered nucleus; m and n = 0 or 1), e.g. the green 3-ethyl-2-(1-ethyl-2-thio-3-indolinylidene)-ethylidene-benzothiazolone, are obtained by condensing a compound of formula—



with one of formula—



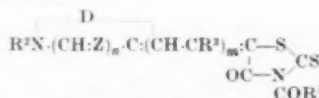
(Q = thioether, thioethervinyl or acetanilidovinyl; X = acid radical) in presence of a basic condensing agent. C.O.C.

### Merocyanine Dyes

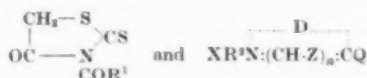
Ilford

BP 829,644

Dyes of formula—



(R<sup>1</sup> = subst. or unsubst. Ar or alkoxy; R<sup>2</sup> = Alk, Ar or aralkyl; R<sup>3</sup> = H, Alk, aralkyl or Ar; Z = N or > CH; m and n = 0 or 1; D = residue of a 5- or 6-membered nucleus), are obtained by condensing together compounds of formula—



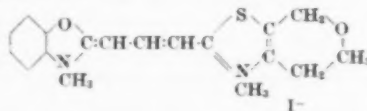
(Q = thioether, thioetheralkenyl or acetanilidovinyl; X = acid radical). Thus 3-benzoyl-5-(1,3,3-trimethyl-2-indolinylidene)ethylidene-2-thiothiazolid-4-one, is obtained by refluxing 2-(acetanilidovinyl)benzoxazolmethiodide and 3-benzoyl-2-thiothiazolid-4-one in alcohol in presence of triethylamine. C.O.C.

### Cyanine Dyes containing a 6,7-Dihydro-4-H-pyrano-(4,3-d)-thiazole Nucleus

Sperry Rand Corpn.

USP 2,899,430

The above bases are first converted into quaternary salts and then treated with 2-halogenoquinoline quaternary salts in presence of an acid binding agent to yield pseudo-cyanine dyes. The 2-halogenoquinoline quaternary salts can be replaced by other quaternary salts to yield other types of cyanine dyes, e.g. 2-alkylmercapto or 2-aryl-mercaptobenzothiazole or naphthothiazole salts yield simple cyanine dyes. Thus 2-methyl-6,7-dihydro-4-H-pyrano(4,3-d)-thiazole metho-*p*-toluene sulphonate refluxed with 2-β-acetanilidovinylbenzoxazolmethiodide in presence of triethylamine and pyridine yields the magenta 1',3'-dimethyl-6'-7'-dihydro-oxa-4'-H-pyrano(4,3-d)thiazolo-carboyanine iodide—



C.O.C.

### Titanium Dioxide (C.I. Pigment White 6)

DuP

USP 2,899,278

When making TiO<sub>2</sub> by oxidation of TiCl<sub>4</sub> vapour the cooling conduit is kept free of deposits of TiO<sub>2</sub> by adding



to the vapour stream  $\text{TiO}_2$  granules obtained by water-washing and baking at 500–900°C. the  $\text{TiO}_2$  dust from a fluid energy mill used for grinding  $\text{TiO}_2$ . C.O.C.

- The Solubility of Wool Dyes—Its Assessment and Practical Significance (VIII p. 323)  
 Reactive Dyes for Nylon (VIII p. 323)  
 New Ideas in the Application of Phthalocyanine Derivatives to Textiles (IX p. 325)  
 Fading of Azo Dyes in Cellulose Acetate Film (XI p. 328)  
 Myrobalans (C.I. Natural Brown 6)—an Important Tanning Material (XII p. 328)

## V—PAINTS; ENAMELS; INKS

### Aspects of Pigment Dispersion related to Usage

I. S. Moll J.S.D.C., 76 (March 1960) 141–150

### Solvents for Acrylic Resins

F. A. H. Watson *Offic. Digest, Fedn. Soc. Paint Technol.*, 32 (Jan 1960) 100–7

Viscosities of resin solutions are quoted for various types of solvents. The lower ketones and aromatic hydrocarbons are the most effective solvents but selection of a solvent system must take account of its effect on film properties, particularly flow. Such considerations indicate a "high-low" system as being the most satisfactory. However, use of substantial quantities of high-boiling solvents in these systems led to solvent release problems and these were examined by comparing the influence of different high-boiling solvents on the drying rate of acrylic lacquer films. The drying rate was measured in terms of film hardness. Formulations are given for suitable solvent systems for acrylic lacquers. C.O.C.

### Trail of the Fugitive Mahogany Varnish Stain

L. D. Soff *Offic. Digest Fedn. Soc. Paint Technol.*, 32 (Jan 1960) 56–66

Brushouts of varnish stain and penetrating stain made with the same amounts of the same mahogany dye when exposed side by side show that the varnish stain may fade noticeably within a few days while the penetrating stain may remain unaffected for several months. As it seemed that the fading may not be caused by the non-volatiles in the varnish other vehicles were tried. One was found in which the mahogany colour remained fast for over a year. This vehicle, a styrenated alkyd, was lower in solids than the original varnish so another varnish series was run with a lower percentage of solids but the fastness was not improved. The styrenated alkyd contained no drier whereas the other vehicles usually had excess. Subsequent work showed (1) the fading was not caused by light, (2) the dye—and others tried—was sensitive to excess Co, as naphthenate or tallate, particularly when the Co is functioning, (3) Pb tallate produced no early fading, (4) Co in a clear prime coat can affect the mahogany dye in the top coat and Co in a clear topcoat can affect the mahogany dye in the prime coat. C.O.C.

### Leaf Stabilisation of Aluminium Paints

R. Rolles

*Paint & Varnish Production*, 49 (10) (1959) 33–8, 98

The mechanism of leafing of Al pigments is discussed and related to (1) their surface films of stearic acid and (2) effects of organic acids present on leaf stability. Leafing stabilisation of acid vehicles by Alcon Stabilizer No. 5 is effected by adding 2.5 mg./acid number/g. vehicle solids of the stabiliser to the vehicle and allowing to stand for 18 hr. before adding the pigments and driers. Al paints so stabilised retain leafing properties for long periods and also show improved durability characteristics. C.O.C.

### Amino Coating Resins

F. Schollick

*J. Oil Col. Chem. Assoc.*, 43 (March 1960) 181–195

A survey of raw materials used in surface coatings with particular reference to the relative properties of melamine and urea resins. Comparison of the ultraviolet absorption spectra and other properties of epoxy and amino resins enables significant deductions to be made about the effect of combining various resins, with resultant improvement in film formation and chemical resistance. C.O.C.

### Effect of Weaker Conditions on the Gloss Retention of an Alkyd Paint Pigmented with R-Titania

E. Oakley

*J. Oil Col. Chem. Assoc.*, 43 (March 1960) 201–213

Exposure of a large number of alkyd gloss paints of identical composition to natural weathering at different times of the year showed existence of a high degree of correlation between gloss retention and measured solar energy above a fixed rate. It was the intensity rather than the duration of sunshine which caused film failure and it is clear that it is this factor which is largely responsible for the ultimate deterioration of gloss paint films. The influence of moisture cannot be directly related to film failure but the weather records show that it plays some part. The work indicated the difficulties that can arise if specifications demand durability trials to be carried out by reference to the calendar without regard for changing weather conditions. C.O.C.

### Adhesion of Latex Paints to Plaster under Humid Conditions

E. Hoffmann

*J. Oil & Col. Chem. Assoc.*, 43 (March 1960) 196–200

The pigment:binder ratio has no influence but storage in humid atmospheres (100% R.H.) decreased adhesion of the film as did alternate wetting and drying. C.O.C.

### Rheology of Carbon Black (C.I. Pigment Black 6 and 7) Suspensions

C. C. Mill

*J. Oil & Col. Chem. Assoc.*, 43 (Feb 1960) 77–95

Examination of suspensions of Carbon Black in printing ink vehicles showed that when freshly milled they behave as simple Bingham bodies. On standing, a structure develops which is progressively destroyed as the rate of shear increases: the new condition of the suspension has at least short-term stability so that a hysteresis loop is obtained if the material is subjected to a shear rate cycle. This structure formation seems to occur in two stages. Immediately after shearing, the structure begins to form and increases with time as indicated by the initial torque immediately on starting to shear the material. This structure is weak and readily destroyed even at low rates of shear. Long standing results in a more rigid structure only fully destroyed by application of extremely severe conditions, e.g. in a three-roll mill. Possibly the weak structure is caused by interparticle forces and the more rigid one by particle agglomerates requiring large forces to disperse them. The flow curve of this type of suspension cannot be described by the two-constant formulae of Bingham and Goodeve and a better fit is obtained with a three-constant equation. C.O.C.

### Water Retention of Latex-bound Pigmented Coating Colours

R. L. Hagerman, R. G. Jahn, and W. H. Somers

*TAPPI*, 42 (Sept 1960) 746–751

The effects of adhesive composition, adhesive level, % solids, type and quantity of synthetic thickener, pigmentation and order of mixing on water retention and other coating colour properties have been studied. The concn. of methyl cellulose is more important than its mol. wt. Methyl cellulose is as effective as sodium alginate. There is no correlation between water retention and pick resistance or viscosity, in contrast to casein. The inclusion of small amounts of synthetic thickener appreciably increases water retention. 12 references. R.A.

### Recent Developments in Polyurethanes

H. A. Hampton, R. Hurd, and H. J. Shearing

*J. Oil & Col. Chem. Assoc.*, 43 (Feb 1960) 96–123

An account of recent advances in the chemistry and technology of polyurethanes. Development of a two-feed spray equipment for application of urethane lacquers and foams is described as is the effect of the composition of urethane films on colour retention, gloss retention, water vapour transmission, low temperature flexibility, and electrical insulation properties. C.O.C.

### Anti-corrosive Water-emulsion Paint for Metal Surfaces especially New Galvanised Steel

D. Frank

*J. Oil & Col. Chem. Assoc.*, 43 (Feb 1960) 140–8

Describes development of an oil-free polyacrylic dispersion paint formulated with a correct pigment-binder ratio to assure durability and containing zinc chromate

to inhibit corrosion. Its preparation entails use of a neutral dispersion and modified manufacturing procedure. It has remarkable durability, versatility, cheapness, ease of application, and opens up a new field in the protection of metal surfaces by corrosion-inhibitive water paints.

C.O.C.

## PATENTS

**Rendering Proteins Resistant to Putrefaction**

Borden Co. BP 826,326

Protein, e.g. casein, containing iron and/or copper impurity, is mixed with a halogen source,  $H_2O_2$ , and a sequestering agent for Fe and Cu. The mixture is kept above 0°C. until reaction between the components is completed, enough water being used to dissolve the halogen source and moisten the protein. The product is resistant to mould growth for several months even when inoculated with a suspension of mouldy casein and saliva, this property being uninfluenced by leaching with hydrocarbon oil or liquid wax. It is compatible over a wide range of conditions with negatively charged latex and clay particles.

C.O.C.

**Pigment Dispersions**

General Aniline BP 827,491

Pigment dispersions of high colour value and of excellent resistance to flocculation, aggregation and agglomeration are obtained by treating an aqueous mixture of a pigment and a non-ionic dispersing agent at 60–100°C. until a well kneading plastic mass results. After mixing is complete the water is decanted off and the mass kneaded until the pigment particle size is 0.1–2.0  $\mu$ . in diameter but mostly < 0.8  $\mu$ . The mass is then either diluted with water until a flowing paste is obtained or it may be dried and ground to yield a water-dispersible powder. Such a powder incorporated in a latex paint imparts maximum brilliance in colour value and there is no flocculation on ageing.

C.O.C.

**Poly-perhalogenocarbon Resin Coatings**

P. R. Welch BP 829,023

**Metallo-organic Compounds for modifying Resinous Films**

Harsco Chemical Co. USP 2,901,452

The precipitate obtained by treating dimethylethanolamine with Zr, Sn, or Al chloride may be dissolved in polyhydric alcohols, e.g. ethylene and propylene glycol, by modifying the precipitate with a trace of water. Such solutions are soluble in water and are used to modify the properties of resinous films obtained from aqueous solution, e.g. to make them harder and more resistant to water.

C.O.C.

**Coating Composition obtained by treating Rubber with Hydrocarbons and Reactive Pigments**

Forman, Ford &amp; Co. USP 2,901,447

Natural or synthetic rubber is milled with (1) a drying oil or a resin binding medium or vehicle and (2) a reactive pigment, e.g. ZnO (C.I. Pigment White 4) till a plastic material of true rubber-like consistency is obtained. The product can itself be used as a protective coating but in addition it is compatible with and freely soluble in all alkyl and oleoresinous paint systems and, when emulsified, with latex paint systems.

C.O.C.

## VI—FIBRES; YARNS; FABRICS

**Degree of Polymerisation and its Distribution in Cellulose Rayons. IX—Influence of Distribution of Degree of Polymerisation on the Mechanical Properties of Monofilaments**

R. J. E. Cumberbirch J. Textile Inst., 50 (Sept 1959) T 528–547

**Moisture Relations of Cellulose. V—Stabilisation of Cellulose and Variation with Temperature of its Heat of Wetting in Water**

M. Wahba and K. Aziz J. Textile Inst., 50 (Oct 1959) T 558–568

The heat of wetting of stabilised and of unstabilised cellulose in water was measured at different temperatures from 0–45°C. by breaking a vacuum-sealed glass ampoule containing a known weight of dry cellulose under the liquid in a calorimeter and measuring the rise of temperature with a thermistor. The cellulose was stabilised by repeated

immersion in water at 60°C. and drying in *vacuo*. Evolution of heat is slower the lower the temperature, indicating that diffusion of water through the cellulose gel is governed by some reaction between them, the rate of reaction increasing with rise in temperature. Stabilisation of cellulose results in reproducibility of its heat of wetting as well as of the sorption isotherms. The heat of wetting of stabilised cellulose decreases with rise in temperature in a way that can be represented by two straight lines meeting at 23°C., the line on the lower temperature side being steeper. The break in the curve denotes the transition temperature which marks the increase of activity of cellulose with rise in temperature and agrees with the same conclusion drawn from sorption isotherms. The heat of wetting-temperature curve of unstabilised cellulose is similar, but less definite, and shows a transition temperature practically the same as that of stabilised cellulose. Stabilisation has no appreciable effect on the heat of wetting below the transition temperature and decreases it at higher temperatures, the decrease being greater the higher the temperature. This effect is discussed in terms of the reorientation of chain molecules in the amorphous regions of the cellulose, in accordance with the effect of stabilisation in displacing the adsorption isotherms.

C.O.C.

**Dyeing Properties of Viscose. III—Effect of Spinning Conditions**

A. Nakai J. Soc. Textile Cellulose Ind., Japan, 15 (May 1959) 422–425

The dyeability of viscose decreases and the surface colour becomes brighter because of ring dyeing under the following conditions: increase in age of the viscose, acid concentration or  $Na_2SO_4$  conc.

L.P.

**Dynamics of Textile Materials. III—Viscoelastic Properties of Wool**

K. Shirakashi, N. Oguchi, and S. Kurita J. Soc. Textile Cellulose Ind., Japan, 15 (May 1959) 388–391

The viscoelastic properties of normal and super-contracted Lincoln wool fibres are measured in water and aq. phenol by a free-vibration type rheometer (period = 10–64 sec. for free vibration) and a constant rate of traverse extensometer. In water, the initial Young's modulus and internal viscosity of super-contracted wool are lower than untreated wool. The Young's modulus also decreases in phenol, suggesting the breakage of weak H bonds by the phenol. These bonds are strongly affected at the initial part of the load-extension curve. Both the Young's moduli and coefficients of internal viscosity at different points in the range of 0–25% extension, decrease in phenol solution but the relaxation times increase.

L.P.

**Thermofixation Effect on Wool**

W. Heydeck Melland Textilber., 40 (Nov 1959) 1327–1328

Wool-polyester fabrics are subjected to dry heat setting. The effect of this on white merino wool is investigated. This was heat set for 15–30 sec. at 160–190°C. Physical properties examined included wet and dry tenacity and extension at break, chemical properties, cystine content, sorption, swelling, urea-bisulphite solubility, and alkali solubility. No significant alterations of physical or chemical properties occurred. It seems that neutral wool is not adversely affected by this treatment.

S.M.J.

**Cystine in Wool. II—Pauly's Reagent for Reduced Wool**

Y. Nakamura and Y. Nemoto J. Soc. Textile Cellulose Ind., Japan, 15 (May 1959) 407–413

The Pauly colorimetric method for estimating damage to wool involves considerable errors caused by reduction of the wool samples. The amount of colour produced by acid-reduced wool decreases as the degree of reduction increases and can be used to estimate it. Treatment of the reduced wool with the diazo salt causes decrease in sulphhydryl group content, alkali solubility and phenol-shrinkage. Comparison between diazo salt and  $H_2O_2$  treatment shows that the former gives a larger alkali solubility and smaller shrinkability than the latter. This appears to be caused by sulphonic groups in the compound and decrease in sulphhydryl groups as a result of phenyl thioetherification by the diazo salt.

L.P.

### Interaction of Swelling Agents with Wool and Nylon

G. King

*Proc. Symposium Colston Research Soc.*  
10 (1958) 322-342

A review, followed by discussion, which covers sorption and solution theories to explain the interaction in these systems and the effects of polymer crystallinity and H bonding. C.O.C.

### Tryptophane content of Weathered Wool and Mohair and Morphologically Deviating Wool

D. P. Veldsman

*Chem. and Ind.*, 27 (4 July 1959) 878-880

The samples (30 mg.) were hydrolysed in a 0.2% solution of freshly crystallised *p*-dimethyl aminobenzaldehyde (10 ml.) in 85% sulphuric acid, at 65°C. After 2-3 hr., the solutions were rapidly cooled, M/10 sodium nitrite (0.1 ml.) was added, and after 20 min. the solution was made up to 25 ml. and the tryptophane content was measured. This rapid method at 65°C gives the same results as Graham's original but slower method at room temp. Tryptophane content is roughly inversely proportional to the fibre diameter for both merino wool and mohair, and decreases on weathering. Copper deficiency results in wool with a tryptophane content lower than that of weathered wool, but cobalt deficiency results in about the same tryptophane content. E.V.T.

### Cross-linking of Cellulose Acetate by Ionising Radiation

S. H. Pinner, T. T. Greenwood, and D. G. Lloyd

*Nature*, 184 (24 Oct 1959) 1303-1304

The normal response of cellulose acetate to ionising radiation is one of degradation. Radiation of cellulose acetate plasticised with 32% triallyl citrate, which may itself be polymerised by this method, using 2-MeV electrons causes two-fold increase in tensile strength even when the radiation dose is  $> 10$  Mrads. Normal plasticisers do not show this effect. The cellulose acetate becomes resistant to acetone, the swelling index being reduced to a minimum of 1.05 at 20 Mrads and the gel fraction increased to 100% at 30 Mrads. There is reduction in concn. of triallyl citrate during these changes and apparently cross-linked cellulose acetate arises from irradiation in presence of a network-forming monomer having a short propagation chain which serves as an efficient trap for polymeric radicals whether produced by radiation or, indirectly, by hydrogen abstraction from the cellulose acetate. F.J.

### Effect of Acid and Alkaline Treatments on Polyester Fibres

G. von Hornuff

*Faserforsch. und Textiltech.*, 10 (Dec 1959) 563-569

Polyester fibres are not hydrolysed by mineral and organic acids below 80°C. Polyester-wool mixtures can be carbonised safely with  $\text{AlCl}_3$  or dry  $\text{HCl}$  but not with  $\text{H}_2\text{SO}_4$ . They are resistant to acid and alkaline milling and to repeated washing treatments of varying severity. Some degradation was observed after mercerising and boiling in  $\text{NaOH}$ . L.A.T.

### Orientation of Polycaprolactam Monofilament and its Resistance to Abrasion

G. Urbanczyk

*Zesz. Nauk. Politech. Łódz.*, 23 (No. 4) (1959) 31-99

The degree of orientation of polycaprolactam monofilament yarn was determined from measurements of its double refraction. Its abrasive resistance was measured on specially designed apparatus, where the filament was brought in contact with a rotating roller, covered with a ceramic. The conclusion reached states that the resistance to abrasion of polycaprolactam filament is a directional quantity. Its longitudinal factor is inversely proportional to its orientation. T.Z.W.

### Transmission of Ultraviolet Radiation by Dyed Fabrics

V. P. Tavelodub

*Tekstil. prom.*, 19 (Nov 1959) 63-65

Investigations with nine different direct dyes have shown that colour has no direct effect on the transmission of ultraviolet radiation (254-365  $\mu$ ). G.J.K.

### PATENTS

#### Crimped Cellulosic Fibres

Joseph Bancroft &amp; Sons Co.

BP 824,399

Tow or yarn is fed continuously against a mass of crimped fibres held compactly in a closed crimping zone. The crimped fibres pass along this zone to a discharge

point but before reaching this point they are impregnated with an agent which when heated reacts with cellulose to fix the crimp, e.g. dimethylolurea. The impregnated fibres are heated sufficiently before leaving the crimping zone that they retain the crimp when the compacting force is released. Complete curing can be effected either before or after the fibres are released. C.O.C.

#### Rendering Polyacrylonitrile Readily Dyeable

Dow Chemical Co.

USP 2,899,262

A polymer containing  $< 85\%$  acrylonitrile is dissolved in an aqueous solution of a salt and then extruded into an aqueous coagulant, the resulting filament stretched and washed to remove saline constituents. Either before or after coagulation and while still an aqua gel and preferably after most of the inorganic salt has been washed out it is treated with an aqueous solution of a salt of polyalkylene amine of mol. wt.  $< 200$ , or its fatty acid amide, or *N*-alkyl or carboxyalkyl derivative, of such an amine or amide, or an aldehyde condensate of such an amine, so as to absorb  $< 1\%$  of the agent, e.g. polyethylene amine tetrastearamide hydrochloride (amine of mol. wt.  $> 1800$ ). The product dyes readily from normal baths with direct, acid, mordant, basic, vat, solubilised vat, disperse, and azoic dyes. Lists of specially suitable dyes in each class are given. C.O.C.

#### 2 - Cyanoethyl - NNN' - tetramethyldiamidophosphate for rendering Acrylonitrile Polymers Flame Resistant

Monsanto Chemical Co.

BP 825,803

Incorporation of 2-cyanoethyl-NNN'-tetramethyl-diamidophosphate—



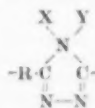
in polymers containing  $< 70\%$  acrylonitrile renders them flame-resistant and of improved flexibility. C.O.C.

#### Aminotriazole Polymers

Gy

BP 824,163

Polymers composed of units of formula—



(R = divalent hydrocarbon; X = H,  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{COOM}$  (M = H or monovalent inorganic cation); Y =  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{COOM}$ ) unlike previous amino triazole polymers, e.g. those obtained according to BP 612,600 (J.S.D.C., 65 (1949) 190) do not tend to form acid salts. Thus fibres formed from them are not unduly sensitive to perspiration. C.O.C.

#### Lowering the Shrinkability of Polyolefine Filaments

Vereinigte Glanzstoff-Fabriken

BP 827,500

Treatment at  $> 90^\circ\text{C}$  with a liquid aromatic, cycloaliphatic or mixed cycloaliphatic-aromatic hydrocarbon of b.p.  $> 110^\circ\text{C}$  for 10-300 sec. is used. C.O.C.

#### Fibre Blends readily dyed to a Solid Colour

Dow Chemical Co.

BP 829,075

A mixture of cotton and/or viscose rayon and an acrylic polymer containing  $< 80\%$  acrylonitrile containing mixed with the polymer  $< 20\%$  of its weight of an *N*-vinyl-3-morpholine or *N*-vinyl-2-oxazolidinone polymer as a dye receptive adjuvant, is readily dyed solid with vat, direct, sulphur, and azoic dyes. C.O.C.

Alkaline Degradation of Alginates (III p. 306)

Antistatic Finish for Textiles (III p. 307)

Mercerising and Wetting Agents (VII p. 322)

Bleaching Viscose Rayon Filaments during their Manufacture (VII p. 322)

Wash-and-Wear Finishing Developments (X p. 326)

Reaction of Keratin Fibres with 1,5-Bis-(chloromethyl)-2,4-xylene and 1,2,4,5-Tetrakis(chloromethyl)benzene (X p. 326)

Compositions for Removing Hair or Wool from Skins (XII p. 329)

Semi-micro Method of High Accuracy for Determining Sulphur in Wool (XIV p. 331)



## VII—DESIZING; SCOURING; CARBONISING; BLEACHING

### Mechanism of Detergency

D. G. Stevenson

*J. Textile Inst.*, **50** (Sept 1959)  $\tau$  548-9

R. P. Harker

*Ibid.*,  $\tau$  549-552

Criticism of a paper by Harker (*J. Textile Inst.*, **50** (1959)  $\tau$  189; *J.S.D.C.*, **75** (1959) 328) and his reply.

C.O.C.

### Use of Trichloroethylene in Continuous Scouring and Bleaching of Textiles. II—Application of Solvent Treatments to Fibres other than Cotton

W. A. S. White, H. J. Ross, and N. F. Crowder

*J. Textile Inst.*, **50** (July 1959)  $\tau$  320-9

Shows that the continuous solvent-extraction technique can be applied with advantage to rayon, linen, wool, jute, and glass fibre fabrics in a convenient, safe, and economic manner.

C.O.C.

### Mercerising and Wetting Agents

M. Rösch

*Melliand Textilber.*, **40** (Nov 1959) 1306-1315

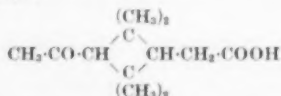
A thorough discussion, with many references, of the history of mercerising and of the relationship between tension, lustre, extension at break, tenacity, concn. of NaOH, temp., and dye uptake, illustrated by numerous graphs. Several continental examples of mercerising plant are depicted. The stability of different wetting agents, their greater solubility in more conc. lye, and NaOH sorption estimates of cotton by back-titration after immersion in HCl are given. Lye sorption and shrinkage often run parallel, but do not always accord well with wetting times, determined in an insufficiently standardised manner. Different wetting agents can act synergistically, but only when mixed in definite proportions. Reliable indications of degree of mercerising are only obtained when several tests are carried out. Iodine and ultraviolet fluorescence after treatment with Naphthol AS-RL (C.I. Azoic Coupling Component 11) only confirm mercerising, baryta titration affords an estimate of degree of mercerising (but is too difficult and liable to error), as does also dyeing with e.g. Sirius Supra Blue G (C.I. Direct Blue 78). Microscope cross-sections of mercerised yarns show that mercerising in practice is usually incomplete, one wetting agent promoting even mercerising of the outer zones only of all fibres in a yarn, another wetting agent complete mercerising of the outer fibres only in a yarn. S.M.J.

### Pinonic Acid as a Mercerising Penetrant

H. B. Summers and G. W. Hedrick

*Amer. Dyestuff Rep.*, **47** (25 Aug 1958) 571-3

Pinonic acid—



a potentially cheap compound derivable from turpentine, when mixed with Butyl Cellosolve is as effective as creasylic acid as a wetting agent in mercerising lyes.

C.O.C.

### Activation of Sodium Chlorite Bleaching Solutions

T. Madlung

*Faserforsch. und Textiltech.*, **10** (Dec 1959) 570-573

Ammonium salts are easily applied and efficient activators. With  $\text{NH}_4$  acetate or formate, pH 4.5-4.8 is constant even at the boil.  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  give pH about 3.4. In all cases a good white and satisfactory exhaustion is obtained.

L.A.T.

### Bleaching Synthetic Fibres and their Blends with Natural Fibres

W. Grunwald

*Z. ges. Textil-Ind.*, **61** (10) (1959) 380-4

*Chem. Abs.*, **53** (1959) 22961

Polyamide fibres are bleached with  $\text{NaClO}_2$  and peracetic acid, polyester fibres with  $\text{NaClO}_2$  and  $\text{NaClO}$ . Acrylic fibres are divided into three groups: (1) those having acid groups, e.g. Dralon and Orlon 42, (2) those with basic groups, e.g. Acrilan, and (3) pure polyacrylonitrile fibres, e.g. Redon. Group 1 are bleached with  $\text{NaClO}_2$  at 98-100°C. at < 90° bleaching is poor,  $\text{NaClO}$  has no bleaching action on these fibres. Group 2 were bleached with conc.  $\text{H}_2\text{SO}_4$  1.5-2.0 g./l., 30-45 min. at 90-5°C., followed by a short

rinse and treatment with 80%  $\text{NaClO}_2$  (1-2 g./l.), Chlorite Stabiliser BASF (1-2 g./l.) and conc.  $\text{H}_2\text{SO}_4$  to bring to pH 2 for 1-0-1.5 hr. at 90-5°C. Group 3 were treated as Group 2 but at 95-8°C.

C.O.C.

### PATENTS

#### Peroxide Bleaching of Cellulosic Fabrics

Food Machinery & Chemical Corpn.

BP 826,094

Bleaching is carried out rapidly by impregnating with 80-125% of the fibres' weight of alkaline 0.5-2.0% (by wt.)  $\text{H}_2\text{O}_2$ , placing in a closed container and steaming under 30-80 lb./sq.in. This yields excellent whites in 1-5 min.

C.O.C.

#### Chlorite Bleaching

Deutsche Gold- und Silber-Scheideanstalt

BP 828,049

Chloral hydrate used as an activating agent when bleaching natural or man-made fibres with an aqueous chlorite has the advantage that it does not liberate chlorine dioxide when the liquor is cold or does so only very slowly. Bleach liquors containing it are stable for several days at room temperature and it is only upon heating or after a long period that activation of the chlorite solution occurs. Generally 5-50% chloral hydrate on the weight of chlorite is used. Addition of a little  $\text{H}_2\text{O}_2$  further improves the stability of the bleach liquor without any deleterious effect on its activation when heated.

C.O.C.

#### Bleaching Viscose Rayon Filaments during their Manufacture

T.M.M. (Research)

BP 826,190

Bleaching, particularly during continuous extrusion of filaments during their manufacture, is effected by successive separate treatments with aqueous acid solutions of an alkali metal permanganate and  $\text{H}_2\text{O}_2$ . The acids used are sulphuric, phosphoric or acetic.

C.O.C.

#### Continuous Scouring of Wool Yarns or Fabrics

ICI

BP 825,402

The material, either in open width or rope form, is given a quick treatment with tri- or perchloroethylene, preferably at b.p., followed, preferably but not necessarily, by a simple squeeze to eliminate much of the entrained solvent, and finally a short treatment with an aqueous medium at a temperature which causes rapid evaporation of the remaining solvent. The process can be made continuous.

C.O.C.

#### Stabilising and Bleaching Knitted Fabrics of Cellulose Triacetate

Celanese Corp. of America

BP 828,096

The fabric is bleached in aqueous medium and either before or during bleaching is treated with an aqueous liquid at < 250°r. Thus warp-knit cellulose triacetate tricot fabric is scoured for 30 min. at 250°r. under 15 lb. pressure with an aqueous solution containing sodium hexametaphosphate (1 g./l.) and soap (1). It is then rinsed twice and bleached for 1 hr. in an aqueous solution at pH 6.5 containing peracetic acid (2.3 g./l.), NaOH (0.85), and sodium hexametaphosphate (0.5) at 260°r. and under 20 lb. pressure. The fabric is held at constant dimensions throughout the process. The resulting fabric has excellent dimensional stability, whiteness, and little tendency either to yellow when exposed to sunlight or nitrogen oxides or to become wrinkled when washed.

C.O.C.

#### Bleaching Nylon

DuP

USP 2,898,179

A mixture of citric acid, an alkali metal chlorite, an alkali-metal nitrate and a buffer to maintain an aqueous solution of the mixture at < pH 7 is used, preferably in presence of a detergent. It does not attack metals. Thus sodium chlorite (0.1 part), citric acid (0.3), sodium nitrate (0.4), anhydrous disodium hydrogen phosphate (0.2), and sodium sulphate (0.04) is dissolved in water (100). The solution has pH 4.5. Nylon treated in the solution for 2 hr. at 70°C. is given a good bleach and loses a little in tensile strength, samples of aluminium and stainless steel in the bath remained unaffected and monel metal was only slightly pitted.

C.O.C.

#### Desizing Glass Fibres

W. Kilby and W. A. S. White

BP 825,507

Simple, rapid, and continuous desizing using solvent extraction and hot water washing removes not only oily and resinous constituents of the size but also starchy and

gummy matters and thus reduces residual organic matter to an acceptable amount. C.O.C.

Effect of Acid and Alkaline Treatments on Polyester Fibres (VI p. 321)

Spraying Liquids or Solids on to Paper, Cloth, etc. (X p. 327)

### VIII—DYEING

#### Kinetics of the Vat Dyeing of Cellulose

M. J. Artym and P. V. Morfyanov

*Tekhnol. tekstil. prom.*, No. 6 (13) (1959) 107–113

Using C.I. Vat Green 1 and C.I. Vat Blue 20 diffusion coefficients were determined by Hill's equation from the degree of exhaustion  $E$  obtained experimentally by dyeing samples of cuprammonium rayon. From the graph of  $E/2$  against  $K$  the diffusion coefficient  $D$  was obtained using  $K = Dt/r^2$ . Having obtained the diffusion coefficient at two temperatures the activation energy was calculated using the equation—

$$\log \frac{D_1}{D_2} = \frac{E}{2.3R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

In a vat containing dye, caustic soda, and Na hydro-sulphite diffusion coefficients were found to be of the same order as those of direct dyes. Dyeing assistants, e.g. pyridine, triethanolamine, and preparation "OP<sub>10</sub>" [ $(C_8H_{17}C_6H_4 - O(CH_2CH_2O)_{10-12} - CH_2CH_2OH)$ ] have the same effect on the diffusion coefficient as when dyeing with direct dyes, i.e. (a) diffusion coefficient increases with the increase in the concentration of the assistant, (b) activation energy of diffusion decrease, (c) there is a change in the degree of aggregation of the leuco compounds in solution. L.S.L.

#### Vat Dyeing of Cotton Fabric by Pigmentation Methods

M. R. Fox and J. F. Mawson

*J.S.D.C.*, 76 (Feb 1960) 73–77

#### The Pad-Roll Dyeing System. A Summary of Experience

R. Kern

*J.S.D.C.*, 76 (March 1960) 173–178

#### The Application of Reactive and Direct Dyes to Rayon Staple by Continuous Methods

R. C. Cheetham

*J.S.D.C.*, 76 (Feb 1960) 95–103

#### The Migration of Non-substantive Dyes on Fabrics and its Relation to Saturation Regain and Fibre Surface Structure

D. Wilson

*J.S.D.C.*, 76 (Feb 1960) 84–94

#### The Solubility of Wool Dyes—Its Assessment and Practical Significance

W. Beal

*J.S.D.C.*, 76 (Feb 1960) 78–83

#### Dyeing Wool with 2:1 Metal Complex Dyes

H. Egli and E. Walther

*Amer. Dyestuff Rep.*, 47 (25 Aug 1958) 574–6

An account of a dyeing procedure which does not damage the fibre, relevant data in connection with the recommended auxiliary products being given. C.O.C.

#### Dyeing of Wool Mixtures with Azoic Dyes

A. I. Levchenko

*Tekstil. prom.*, 19 (Nov 1959) 60–63

Wool-cellulose union fabrics have been dyed with various azoic combinations to give deep, medium, and pale dyeings. Fastness properties of seven bases with 2,7-dihydroxy-1,4-naphthoquinone, with and without chrome aftertreatment, are tabulated. G.J.K.

#### Hair Colouring—Modern Formulation Considerations

R. I. Goldemberg

*J. Soc. Cosmetic Chemists*, 10 (1959) 291–306

*Chem. Abs.*, 54 (10 Jan 1960) 826

Review, 31 references. C.O.C.

#### Binding of Dyes by Soluble Wool Keratin Derivatives

B. S. Harrap

*J. Colloid Sci.*, 14 (1959) 300–7

*Chem. Abs.*, 53 (25 Nov 1959) 22959

The binding between acid dyes and water-soluble keratin derivatives was determined by equilibrating aqueous dye liquors of different lengths with solutions of the keratin derivatives contained in bags of dialysis tubing. The amount of dye bound corresponded to the amount needed to neutralise the basic side chains from the lysine

and histidine components of the keratin derivatives. The arginine basic side chains apparently took no part in the dyeing reaction. C.O.C.

#### Dyeing Wild Silk. XIX—Relationship between Amounts of Dye on the Fibre and its Breaking Properties

G. Aida and M. Mitsuishi

*Shinshu Daigaku Sen Igakubu Kenkyu Hokoku*

(1958) 127–9

*Chem. Abs.*, 54 (10 Jan 1960) 904

Orange II (C.I. Acid Orange 7) was adsorbed more with decreasing pH on yamamai silk in the pH range 5–2, while it was adsorbed less from baths containing KCl even at pH 7 or higher. The tensile strength and elongation of the fibre decreased sharply when the dye adsorption reached 0.35 meq./g. and then dropped to 11.87 g. from the initial 14.62 g. in strength and to 0.5–21.1% in elongation when the adsorption reached 0.418 meq./g. The Orange II is apparently adsorbed on the amino group at first and then, when these are all saturated, it is adsorbed on the less active amide site of the polypeptide chain. C.O.C.

#### Dyeing of Cellulose Acetate. VII—Colour and Temperature in Dyeing

K. Odajima

*J. Soc. Textile Cellulose Ind. Japan*,

15 (May 1959) 426–429

Study of the position of the maximum purity point on the luminosity curve showed that more brilliant colours are generally obtained at lower temperatures. This is apparently caused by higher concentration of dye at the fibre surface. L.P.

#### Vapour-phase Dyeing with Disperse Dyes

C. L. Bird, F. Jones, and R. S. Bradley

*J.S.D.C.*, 76 (Feb 1960) 114

#### The Dyeing of Cellulose Acetate with Disperse Dyes. VIII—Determination of Fibre Saturation Values

C. L. Bird, H. K. Partovi, and G. Tabbron

*J.S.D.C.*, 75 (1959) 600–604

#### Reactive Dyes for Nylon

D. F. Scott and T. Vickerstaff

*J.S.D.C.*, 76 (Feb 1960) 104–114

#### Dyeing Synthetic Fibres. 7—Increasing the Dyeability of Nitron (Polyacrylonitrile) by Treatment with Aqueous Calcium Chloride and Zinc Chloride

E. S. Roskin, A. A. Kharkharov, and V. S. Fel'

*Tekhnol. tekstil. prom.*, No. 6 (13) (1959) 104–106

Nitron fabric was treated in a saturated solution of  $CaCl_2$  and  $ZnCl_2$  (6:4) at 80°C. for 30 min. and liquor ratio 75:1. After being thoroughly washed the samples were dyed with acid and direct dyes. The best dyeing method was: 50:1 liquor ratio, dye at 90–92°C. for 1 hr. in presence of 25% of common salt on the weight of goods. This treatment is said to increase the dyeability of Nitron 15 to 20 times, but still allows only for production of pale and medium dyeings. L.S.L.

#### Continuous Dyeing of Synthetic Fibres and Blends

J. J. Iannarone and W. J. Wygant

*Amer. Dyestuff Rep.*, 47 (25 Aug 1958) 585–7

The pad-steam method is particularly recommended for nylon, acrylic, and modified acrylic fibres and their blends with other fibres. The Thermosol method is most suitable for Dacron polyester fibre. Brief references are made to the Pad-Roll, fluid bed, and solvent methods. C.O.C.

#### Mechanism of Dyeing Orlon 42 Acrylic Fibre

T. Vogel, J. M. A. DeBruyne, and C. L. Zimmerman

*Amer. Dyestuff Rep.*, 47 (25 Aug 1958) 581–4

Equilibrium studies support the theory that Orlon 42 is dyed on specific anionic sites by cationic dyes. Relative affinity measurements show that hitherto available dyes have very high affinity for Orlon 42 and so are bad levellers. However, these high affinities are also associated with poor rates of exhaustion, and microscopical cross-sections show incomplete penetration of dye into the fibre. A new class of cationic dyes has lower affinity for and so better levelling on Orlon 42 and also have excellent rates of exhaustion and quickly reach equilibrium. Microscopical cross-sections show that they penetrate completely within normal dyeing time. Their lightfastness ratings are not less than 80 hr. C.O.C.



**Dyeing Acrylic Fibres**

N. Takahashi and Z. Yoshida

*Senshoku to Kako*, 5 (1959) 181-190*Chem. Abs.*, 54 (25 Jan 1960) 1856

Addition of 2% Al, Cr or Sn chloride to acid or direct dyebaths results in better exhaustion, deeper dyeings, and good fastness properties. Stannic chloride gives the best results. The bath must be slightly acid and at  $> 90^{\circ}\text{C}$ .

C.O.C.

**Dyeing Saran Fibre with Acid Dyes**

N. Takahashi and Z. Yoshida

*Senshoku to Kako*, 4 (1959) 1-11*Chem. Abs.*, 54 (25 Jan 1960) 1857

Poly(vinylidene chloride) fibre (Saran) was dyed more deeply at pH 4 with addition of 3-5% of Al ( $\text{NO}_3$ )<sub>3</sub> or Pb ( $\text{NO}_3$ )<sub>2</sub>. A mixture of 3% Al ( $\text{NO}_3$ )<sub>3</sub> and 3% Pb ( $\text{NO}_3$ )<sub>2</sub> was effective with a variety of acid dyes. Saran and wool blends are dyed uniformly by this method.

C.O.C.

**Dyeing Poly(vinyl Alcohol) Fibre**

S. Koshikidaka, S. Niino, and Z. Yoshida

*Senshoku to Kako*, 3 (1957) 145-154*Chem. Abs.*, 54 (25 Jan 1960) 1857

Preliminary treatment with 4% phenol increases take up of direct dyes, e.g. dyeings with Direct Blue BB are twice as deep. Addition of  $\text{FeSO}_4$ ,  $\text{NiSO}_4$  or  $\text{MnCl}_2$  to the dyebath also results in deeper dyeings. Acid dyes containing more than one sulphonate group are unsuitable for use by this method.

C.O.C.

## PATENTS

**Dyeings of Improved Fastness with Direct Metal-complex Azo Dyes**

Ciba

BP 823,405

Dyeings made with direct metal-complex (Co, Ni or Cu) azo dyes on cellulosic materials in presence of an alkylene diamine containing an oxyalkyl group, e.g. 1:2-di-( $\beta$ -oxyethylamino)-ethane tetrasodium phosphate, and aftertreated with a suitable nitrogenous agent, e.g. condensate of 2 mol.  $\text{HCHO}$ , 2 mol. diacyandiamide and 1 mol. ethylene diamine hydrochloride, have better wet fastness than dyeings similarly aftertreated but made in absence of the amine and phosphate.

C.O.C.

**Metallising Azoic Dyeings and Prints in Presence of Oxidising Agents**

General Aniline

USP 2,893,814

When development of an azoic dye or print is carried out in presence of a metal (especially copper) compound with a view to improving its fastness, the tendency for free metal to be deposited on the fabric or machinery can be eliminated by incorporating a soluble oxidising agent, e.g.  $\text{Na}_2\text{Cr}_2\text{O}_7$  or  $m$ -nitrobenzenesulphonic acid in the coupling component solution, which also contains the metallising agent.

E.S.

**Dyeing Protein Fibres with Azo Dyes containing Sulphonfluoride groups**

ICI

BP 824,690

Dyeing is best carried out at a relatively low temperature while treating with an alkaline substance. Thus the yellow dye 3-aminobenzenesulphonfluoride  $\rightarrow$  1-(4-sulphon-phenyl)-3-methyl-5-pyrazolene (3) is dissolved in water (4000) at  $20^{\circ}\text{C}$ . and scoured silk (100) worked in the solution.  $\text{Na}_2\text{SO}_4$  (100) is added during 30 min. and aq.  $\text{Na}_2\text{CO}_3$  (8) gradually added. Dyeing is continued for another hour. The silk is then boiled in an alkaline detergent solution for 10 min. The resulting dyeing has excellent wet fastness.

C.O.C.

**Dyeing Protein Fibres**

ICI

BP 826,376

Better levelling is obtained with water-soluble azo or anthraquinone dyes having a  $s$ -triazinylamino group containing at least one halogen atom as substituent in the triazinyl nucleus, if dyeing is carried out at  $> 55^{\circ}\text{C}$ . in presence of  $> 3\%$  of an acid-binding agent. Thus silk dyed with the dye obtained by treating 1 mol. 2-(4'-amino-2'-methylphenylazo)-naphthalene-4,8-disulphonic acid with 1 mol. cyanuric chloride is a bright yellow of very high fastness to light, degumming, and other wet processes. The silk is entered into the bath, containing only the dye, at  $25^{\circ}\text{C}$ . and  $\text{NaCl}$  gradually added during 30 min. after which  $\text{Na}_2\text{CO}_3$  is added over 30 min., dyeing, still at  $25^{\circ}\text{C}$ .

continued for a further 15 min. and the silk then cleaned for 15 min. with a non-ionic detergent at  $100^{\circ}\text{C}$ .

C.O.C.

**Dyeing Silk and Polyamide Fibres**

ICI

BP 826,375

The fibres are treated with an aqueous solution of a water-soluble azo or anthraquinone dye containing a 4,6-dihalogeno- $s$ -triazinyl-2-amino group and at least one ionogenic solubilising group. Thus the dye orthonilic acid  $\rightarrow$  1-(4,6-dichloro- $s$ -triazinyl-2-amino)-8-hydroxy-naphthalene-3,6-disulphonic acid dyes nylon staple fibre a bright red of very high fastness to washing and wet processing and good fastness to light. It is applied from a bath containing  $\text{NH}_4$  acetate started at  $40^{\circ}\text{C}$ ., raised gradually to  $95^{\circ}\text{C}$ . and exhausted with  $\text{HCOOH}$ , rinsed, and cleansed with a non-ionic detergent for 15 min. at  $65$ - $70^{\circ}\text{C}$ .

C.O.C.

**Increasing the Fastness of Dyeings on Natural Protein, Cellulose Derivative, and Synthetic Polymer Fibres**

ICI

BP 825,017

Dyeings made with dyes containing at least one amino group a H atom of which is readily replaced by treatment with cyanuric chloride at  $20^{\circ}\text{C}$ . in aqueous medium, are given improved fastness to sublimation, wet processing, and burnt gas fumes if the fibres are treated before, during or after dyeing with an aqueous dispersion of a water-insoluble compound containing a mono- or dihalogenated 1,3,5-triazine ring. Thus acetate rayon is dyed with tetraminoanthraquinone (C.I. Disperse Blue 1) and then treated for 1 hr. at  $85^{\circ}\text{C}$ . in an aqueous dispersion of 2,4-dichloro-6-anilino-1,3,5-triazine. The treated dyeing is much faster to wet processing and burnt gas fumes than the untreated dyeing.

C.O.C.

**Cross-dyed Effects on Material containing Fibres of Cellulose and of Cellulose Esters of Low Hydroxyl Content**

Celanese Corp. of America

BP 824,398

The material is mercerised, preferably after being heat set, and then vat dyed. This results in the cellulose being dyed but not the cellulose ester.

C.O.C.

**Dyeing Polyester Fibres with Disperse Dyes**

FH

BP 828,924

More stable dispersions and consequently more level dyeings are obtained if a surface-active phosphoric ester, particularly an orthophosphoric ester, is present in the dyebath, e.g. 2-10 g./l. of the tertiary phosphoric ester of the condensate of 1 mol. dodecylalcohol and 4 mol. ethylene oxide.

C.O.C.

**Dyeing Tightly Wound Glass Fibres Sized with a Water-swellable Material**

Owens-Corning Fiberglass Corp.

USP 2,900,275

Glass fibres sized with gelatin are treated with a spirit-soluble metalliferous substituted guanidine salt of an azo dye. Presence of a Werner complex compound in the dye solution renders the dyed fibres fast to wet processing. Thus gelatin-sized glass fibres are dyed with a solution made up by first adding stearato chromic chloride (30%) in isopropanol (1.5 gal.) to methylricinoleate (2.5) at  $225^{\circ}\text{F}$ . and allowing to cool. The di- $o$ -tolylguanidine salt of the dye 1-amino-2-naphthol-4-sulphonic acid  $\rightarrow$  1-naphthol-8-sulphonic acid having Cr as the metal component (4.6 lb.) is dissolved in methanol (14 gal.) and water (1) and the stearato chromic chloride ricinoleate mixture added to it. The containers of the ricinoleate and stearato chromic chloride are rinsed out with methanol (6) and the solution added to the dye liquor. Finally salicyl anilide (25 g.) is added. This yields a dyeing which is fast to wet processing, rubbing, and bleeding.

C.O.C.

The Remazol Linkage (IV p. 308)

The Solubilities and Heats of Solution of Disperse Dyes in Water (IV p. 309)

Oxidation Bases (IV p. 313)

Aspects of Pigment Dispersion related to Usage (V p. 319)

Rendering Polyacrylonitrile Readily Dyeable (VI p. 321)

New Ideas in the Application of Phthalocyanine Derivatives to Textiles (IX p. 325)

Fading of Azo Dyes in Cellulose Acetate Film (XI p. 328)

Identification of Remazol (FH) Dyes on the Fibre (XIV p. 331)

## IX—PRINTING

## Properties of Thickening Agents and Printing Pastes—II

F. I. Sadov and Sin Men Khen

Tekhnol. tekstil. prom., No. 6 (13) (1959) 91-97

Viscosity of thickening agents consists of two components, (a) viscosity due to structural properties of thickening agents, (b) residual or final viscosity of a paste after its thixotropic characteristics have been destroyed by mechanical action during printing. The final viscosity of a printing paste depends on the type of thickener used. The relationship between structural viscosity and time has been examined. In the case of tragacanth, dextrin, and silicate-starch thickeners the viscosity remained constant for 13 hr. Starch alone increases in viscosity with time because of the relatively slow structural rearrangements in starch solution. The reaction between various components of printing pastes caused gradual drop in viscosity with time. Addition of small quantities of dextrin to starch caused a very rapid drop in viscosity, whilst changes caused by addition of tragacanth were considerably smaller.

L.S.L.

## New Ideas in the Application of Phthalocyanine Derivatives to Textiles

F. Gund

J.S.D.C., 76 (March 1960) 151-158

## Recent Advances in Textile Printing with special reference to Calcium Sulphoxylate Formaldehyde

R. J. Hannay

J.S.D.C., 76 (Jan 1960) 11-15

PATENTS

## Printing Cellulosic Textiles

ICI

BP 824,120

Modification of BP 798,121 (J.S.D.C., 74 (1958) 792) after the dye has been printed on, the printed material is treated with an aqueous solution of an acid binding agent, dried, and washed. Thus an aqueous printing paste containing dye, urea, and Na alginate is applied to cotton cloth, dried, and then passed through a padding mangle with the printed side of the cloth against the lower padding roller. This roller dips into an aqueous solution containing 2%  $\text{Na}_2\text{CO}_3$  and 0.4% alginate. It is then dried over cans, soaped, rinsed, and dried.

BP 824,121

Modification of BP 797,946 (J.S.D.C., 74 (1958) 714) by applying the dyes in a printing paste and aftertreatment as described above.

C.O.C.

## Printing Tufted Fabrics

Stalwart Manufacturing Co.

BP 827,432

A driven roller has a continuous impervious surface covered with a material which readily absorbs dye, e.g. felt, this material forming the pattern to be printed. The absorbent material is continuously charged with dye as the tufted fabric comes into contact with the roller during printing.

C.O.C.

## Printing Polyester or Cellulose Triacetate Fibres with Disperse Dyes

FH

BP 827,731

The dyes are applied in a paste containing a polyhydric alcohol or an ester or ether thereof, dried, and then baked at 140-220°C. Thus polyester fibre cloth is printed with a paste containing the disperse dye 1-amino-2-methoxy-4-hydroxy anthraquinone, water, thiodiglycol, thickener, and the primary orthophosphoric ester of the condensate of 1 mol. dodecyl alcohol and 4 mol. ethylene oxide. The printed fabric is dried, heated in air for 30 sec. at 200°C., rinsed, soaped at 70°C., rinsed, and finished. The resulting print has much greater intensity than one similarly made in absence of the phosphate.

C.O.C.

## Printing Triacetate Rayon

Colanese Corp. of America

BP 825,142

Textiles of a cellulose ester of low hydroxy content, e.g. cellulose triacetate, are printed with an aqueous paste containing a disperse dye and  $\beta$ -phenoxyethanol,  $\alpha$ -phenylethanol or  $\beta$ -phenylethanol, dried, and the print fixed by either steam or dry heat. This gives good colour value and reproducibility of prints.

C.O.C.

## Pigmented Oil-in-water Emulsions yielding Prints of Improved Resistance to Abrasive Laundering

Gy

USP 2,900,354

Increasing the quantity of organic solvent-soluble aminoaldehyde resin to 18-35% of the total binder results in prints of better fastness to rubbing.

C.O.C.

## Screen Printing to Produce Self-supporting Prints

Associated Trapnax

BP 827,063

A viscous dispersion of a thermoplastic polymer of high mol.wt. in a plasticiser is screen printed on to a temporary support. The print is then heated until the dispersion is converted to a coherent plastic film which is then separated from the temporary support either as a coherent whole or together with a second temporary or a permanent support.

C.O.C.

## Diazotype Material

H. D. Murray

BP 825,361

A porous or fibrous base is coated with a suspension containing both unburst starch grains and water-soluble starch or a derivative thereof and then the diazotype layer containing  $\text{SiO}_2$  is applied. The resulting material yields prints of enhanced density, contrast, and fastness to rubbing.

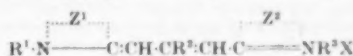
C.O.C.

## Improving the Photosensitising Properties of Some Cyanine Dyes

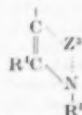
Kodak

BP 828,069

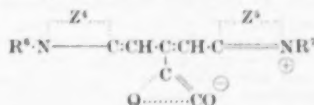
Presence of a water-soluble salt of Cd or Zn improves the photosensitising properties of dyes of formula—



( $\text{R}^1$  and  $\text{R}^3$  = subst. or unsubst. Alk; X = acid radical;  $\text{Z}^1$  and  $\text{Z}^2$  = atoms to complete a 5-membered ring;  $\text{R}^2$  = subst. or unsubst. Ar, thienyl or—



$\text{R}^4$  = H, Alk or Ar;  $\text{R}^5$  = H, Alk cycloalkyl or Ar;  $\text{Z}^2$  = atoms to complete a 3-indolylbenz-3-indolyl or, when  $\text{R}^4$  and  $\text{R}^5$  do not each = H, a 3-pyrryl group, or  $\text{R}^4$  +  $\text{R}^5$  +  $\text{Z}^2$  = atoms to complete a pyrrocolyl nucleus) e.g. 3,3'-dimethyl-9-phenyl-4,5,4',5'-dibenzothia-carboaniline bromide. The effect is still further increased if there is also present a non-ionised dye of formula—



( $\text{R}^6$  and  $\text{R}^7$  = Alk; Q = atoms to complete an indandione or a 5- or 6-membered heterocyclic nucleus;  $\text{Z}^3$  = atoms to complete a 5- or 6-membered ring;  $\text{Z}^4$  = atoms to complete a naphthothiazole or naphthoselenazole nucleus) e.g. 5-[di(1-ethyl-2- $\beta$ -naphthothiazolylidene)isopropylidene]-1,3-di( $\beta$ -methoxyethyl) barbituric acid.

C.O.C.

## Diazotype Material

S.A.R.L. "S.A.P.H.I." Société Alsacienne de Papiers Héliographiques Industriels

BP 828,386

Coating the base sheet with a water-insoluble metal fluoride of particle size 0.01-0.5  $\mu$ , before applying a diazotype coating yields a material giving prints of increased density without any loss in the sensitivity of the coating.

C.O.C.

## Leuco Phthalocyanine and Diazo Compounds in Light-sensitive Coatings

DuP

USP 2,884,326

An organic solvent solution of a phthalocyanine intermediate complex (leuco phthalocyanine) and a 1,2- or 1,4-aminohydroxy- or dihydroxybenzene or naphthalene is used. Thus paper was dipped in an ethanolic solution of the Cu phthalocyanine propigment described in USP 2,662,897 (J.S.D.C., 71 (1955) 558) and 1-methyl-2-diethyl-aminobenzene-5-diazonium fluoroborate, and dried at room temperature, all operations being carried out under orange light. The sensitised paper was exposed to a mercury lamp through a negative. The exposed paper was then washed with ethanol to remove undecomposed propigment and with water to remove unchanged diazonium salt. This yielded a blue print on a white ground.

C.O.C.

**Pressure-rupturable Microscopic Fluid-containing Capsules for use in Printing by Magnetic Means**  
National Cash Register Co. BP 828,983

**Heat-sensitive Copying Sheet**  
Minnesota Mining & Manufacturing Co. BP 829,001

Oxidation Bases (IV p. 313)

Aspects of Pigment Dispersion related to Usage (V p. 319)

Metallising Azoic Dyeings and Prints in Presence of Oxidising Agents (VIII p. 324)

Spraying Liquids or Solids on to Paper, Cloth, etc. (X p. 327)

Coating Fluorinated Polymer Surfaces to make them Readily Wetted by Inks (XIII p. 329)

Analytical Densitometry for Colour Print Evaluation (XIV p. 331)

## X—SIZING AND FINISHING

**Removal of Metal Ions from Cotton Fabrics**  
AATCC Rhode Island Section

*Amer. Dyestuff Rep.*, 48 (26) (28 Dec 1959) 27-36  
At room temperature sodium tetrphosphate is the most effective chelating agent for removal of cations from cotton but at the boil the organic chelating agents are much more effective, ethylene diaminetetracetic acid being the most efficient of those tested. C.O.C.

**Wash-and-Wear Finishing Developments**  
H. Enders *Melliand Textilber.*, 40

(Nov 1959) 1315-1326; (Dec 1959) 1454-1462  
The chemistry of finishing cellulose is discussed in very great detail, particular attention being given to mesomeric and electromeric formulations and reaction mechanisms of condensation. These are used to explain the different characteristics of cellulose cross-linking agents, e.g. reactant resins, and self-condensing resins, the extent to which their behaviour overlaps, and differences in buffering capacity, stability, relative tendency for covalent or hydrogen bond formation, and other properties such as chlorine retention. Chemical entities thus discussed include urea- and melamine-formaldehyde condensates, triazones, other triazine derivatives, hydantoin and acetone resins, reactive resins ranging from ethylene- and acetylene-urea to dimethylolbutanediolurethane, epoxy resins, and acetals. Resin-free finishes are then discussed, and the effect of acids, alkalis, salts, complex compounds and -onium derivatives on cellulose. Acetylation, other esterifying and etherifying reactions, amination, chrom-stearate complexes, siloxanes, and aldehydes are also considered. Infrared evidence is adduced to show greater covalent bond formation with reactive than with urea- or melamine-formaldehyde resins. Photographic techniques employing resin containing radio-active carbonyl carbon demonstrate differential resin distribution in finished fabrics on the surface of yarns, coupled with uniform distribution within individual fibres, and an explanation involving the drying processes is offered. Autoradiographic methods are also utilised to obtain estimates of the wash-resistance of different resins, but are considered excessively expensive for large scale application. A thorough examination of the relative merits of resin and resin-free finishes—e.g. modification of cellulose with bifunctional aldehyde—follows. Testing methods are critically compared with performance in practice, and the unreliability of both wet and dry crease recovery angles and swelling is demonstrated. Experimental data are given which account for this, by showing initial decrease followed by subsequent increase of crease recovery angles with increasing moisture content of both cotton and rayon. Minima occur at 30-50% with rayon, at 20-30% moisture with cotton, both unfinished and finished with alkali, resin-free modifications, and reactive resin. With the latter the minima are least pronounced, which accounts for its better performance, as the damp crease resistance, in contrast to dry or wet crease resistance, is very important, especially if tumbler drying is involved. Reactant resins are at present most efficient, but strength loss is unavoidable. Differences in plastic and elastic extensibility of different resin treatments are elucidated in connection with their bearing on tensile strength, tear strength, and abrasion resistance. After a very detailed consideration, for different types of resins, of formation of

fishy odour due to methylamines, chlorine retention, chlorine damage, browning and other discoloration, wash resistance, effect on lightfastness, and physiological effects, the merits of a blend of ethylene-urea-triazine-epoxy resin catalysed with zinc fluoroborate are stressed. After reviewing older theories, an explanation is given of the opposite effect of resin finishing on tensile strength of cotton, which is diminished, and rayon, which is increased. This is largely based on measuring tensile strength at varying moisture contents. With cotton strength initially increases, with rayon it initially decreases with increasing moisture content, partly because of differences in degree of polymerisation and crystallinity. As resin finishing reduces moisture content at a given relative humidity in a similar manner for both types of cellulose, the observed opposed effects result. A brief discussion of polymeric products designed to improve abrasion resistance follows, with a warning concerning dirt retention, and some recipes are given. There are 70 illustrations and 51 references. S.M.J.

**Self-smoothing Cellulosic Fabrics**

J. T. Marsh *J.S.D.C.*, 76 (Jan 1960) 23-37

**Reaction of Keratin Fibres with 1,5-Bis(chloromethyl)-2,4-xylene and 1,2,4,5-Tetrakis(chloromethyl)benzene**

H. Zahn and H. Steurle *Ann.*, 622 (1959) 175-180  
*Chem. Abs.*, 54 (10 Jan 1960) 370

Treating reduced wool with these benzyl halides leads to cross-linking through cysteine residues. C.O.C.

**Seersucker Effects in Wool Fabrics**

D. Sims and J. B. Speakman *J. Textile Inst.*, 50 (July 1959) T 473-4

Washable seersucker effects in an all-wool fabric were obtained by impregnating with a 1% solution of sodium metabisulphite in a 37:63 by vol. mixture of ethylene glycol and water. The fabric was then treated in a heavy-duty compressive-shrinkage machine having a heated top roller, grooved at right-angles to the axis. C.O.C.

**The Permanent Creasing of All-wool Fabrics**

M. A. Wolfram and J. B. Speakman *J.S.D.C.*, 76 (March 1960) 169-173

**Air-permeable PVC Coated Fabric for Upholstered Furniture.** BS 3217:1960

British Standards Institution. Price 7s 6d.

Specifies requirements for air-permeable PVC coated fabrics corresponding in usage to Grade B fabrics specified in BS 2601, but with the coating porous, perforated or discontinuous. Minimum requirements and methods of test are specified for weights of cloth and coating, coating adhesion, air permeability, breaking load, flex cracking, tear strength, surface drag, heat ageing, and colour fastness. Recommendations in the application and use of air-permeable coated fabrics and on methods of cleaning are given in an appendix. C.O.C.

## PATENTS

**Treating Cellulosic Textiles with Ethylene Urea-Formaldehyde Condensates**

American Cyanamid Co. USP 2,898,238

An aqueous solution at pH 1.0-3.5 containing an ethylene urea-formaldehyde condensate and an acid catalyst of ionisation constant  $\leq 10^{-3}$ , e.g.  $H_3PO_4$ , is applied so that 5% solids are deposited on the fibres which are then dried and baked for 3 min. at 225°C. This gives excellent crease recovery and dimensional stabilisation. C.O.C.

**Resin Finishing of Cotton Cloth**

Tootal Broadhurst Lee Co. BP 827,647

The cloth is treated with a lubricant containing an amide group and a precondensate of 1.8 mol. HCHO and 1 mol. urea (formed by adding 8.8% (on weight of urea) 0.880  $NH_4OH$ ), dried, and baked. Thus formalin (138 parts by wt.) (40 g. HCHO/100 cc.), urea (50), and 0.880  $NH_4OH$  (4.4) were heated together to 30°C. and stood without further heating for 12 hr. Ammonium dihydrogen phosphate (5) was then added and the mixture diluted with water to bring it to s.g. 1.07. Monomethylol stearamide (2), previously made into an aqueous emulsion, was added to the mixture (100). Cotton shirting poplin having a singles weft was impregnated with 60% of this solution, dried, and baked for 3 min. at 135°C. and finally treated with 0.5% aq.  $Na_2CO_3$  at 90°C. for 60 sec., rinsed, and



dried. The finished fabric had good strength against ripping, and required less ironing after washing than the untreated fabric or a similar fabric treated simply with a 1-6:1 formaldehyde-urea resin. C.O.C.

#### Delustring

Tootal Broadhurst Lee Co.

BP 827,646

Textiles, of any type of fibre, are successively impregnated with an aqueous solution of an acid salt of a polybasic acid of dissociation constant  $< 10^9$  and an aqueous solution of a salt with an acid stronger than the polybasic acid of a metal of which a less acid salt with the polybasic acid will just separate out from an aqueous solution of acid salt on removal of water therefrom. The amount of acid salt applied by the first impregnation and the concentration of the second bath are such that separation of much less acid salt occurs during the second impregnation. One of the solutions contains an amino-aldehyde precondensate. Finally the material is dried. Thus a viscose rayon fabric was printed with a vat printing paste, aged, dried, and then impregnated with aqueous dihydrogen sodium phosphate, dried, and again treated with an aqueous solution containing lead nitrate and a urea-formaldehyde precondensate, dried, and baked at 140°C. for 3 min. The fabric was then treated with Na perborate to complete oxidation of the vat dye, and immersed for 15 min. in 0-75% HCl at 20°C. to ensure complete relustring of the printed areas and finally soaped. After drying a lustrous printed pattern on a delustrated ground was obtained and the fabric had good crease-recovery. C.O.C.

#### Rendering Rayon resistant to discoloration during Steam Sterilisation

Johnson & Johnson

BP 828,913

Treatment of a neutral aqueous solution of a salt of a Group IA metal of at.no.  $> 10$  or Group IIA metal of at.no.  $> 19$  greatly reduces any change in colour when rayon is steam sterilised. C.O.C.

#### Wash-and-Wear Finish for Rayon Fabrics

Courtaulds

BP 825,608

Fabric containing  $< 50\%$  by weight of rayon is treated with aqueous NaOH ( $< 5\text{ g./100 cc.}$ ) for  $> 10$  sec. and immediately mangled, washed free of alkali, dried, and then given a crease-recovery finish. The strength and temperature of the dye and the time of immersion is so adjusted, if necessary, by addition of an electrolyte, that the liquor take up of the rayon after being mangled is 150-175% of its oven-dry weight. C.O.C.

#### Flame-resisting Cellulosic Textiles by use of Phosphorus Trisocyanate or Phosphoryl Trisocyanate

Olin Mathieson Chemical Corpn.

USP 2,898,180

Phosphorus trisocyanate,  $\text{P}(\text{NCO})_3$ , and phosphoryl trisocyanate  $\text{PO}(\text{NCO})_3$  impart excellent flame- and glow-resistant properties to cellulosic textiles without causing any loss of tensile strength. Thus cotton cloth padded with 80% of its weight of a 10% solution of phosphoryl diisocyanate in benzene, dried and baked for 2-3 min. at 265°F. had excellent flame- and glow-resistance even after being washed in 10% aq.  $\text{Na}_2\text{CO}_3$ . C.O.C.

#### Setting Keratinous Fibres

National Lead Co.

BP 823,471

The fibres are brought into the desired configuration, destabilised, e.g. with thioglycerol, and then set by treatment with an aminoalcohol titanate or zirconate. Thus hair wound on a mandrel is treated for 45 min. at room temperature in 0-6% aqueous thioglycerol adjusted to pH 9 with ammonia. The hair was then rinsed and treated with an aqueous solution containing 5% of normal triethanolamine titanate and 0-5%  $\text{H}_2\text{O}_2$ , the latter being used to destroy the smell of the mercaptan. C.O.C.

#### Waving Hair in Acid Medium

W. Richter

BP 824,426

Aqueous solutions of esters of sulphydryl carboxylic acids with alcohols containing additional hydrophilic groups are used at pH 1-7 for waving hair. Suitable esters are glycol monothiolglycollate, 1,3-propyleneglycol monothiolglycollate, glycerine monothiolglycollate, lactic acid thiolglycollate, and glycolmonothiolglycollate. C.O.C.

#### Bromate- or Chlorite-urea Oxidative Fixing Composition for Setting Keratinous Fibres

V. McGoldrick and E. G. McDonough

USP 2,899,965

Use of a chlorite or bromate, preferably Na chlorite or bromate, as the oxidising agent in fixing reduced keratinous fibres, gives quicker and more complete fixation than the hitherto used oxidising agents. Skin irritation and the danger of explosion or fire in using chlorites or bromates is obviated by adding urea or sodium lactate to the solution. C.O.C.

#### Heat Shrinking of Synthetic Continuous Filament Webs

Firestone Tire & Rubber Co.

BP 822,809

The material, e.g. tire cord or fabric, is stretched at 320-450°F. and the tension on it relaxed to allow it to shrink at a lower temperature, preferably 150-180°F. C.O.C.

#### Setting of Tubular Fabrics of Man-made Fibres

Adshad & Geeson

BP 826,858

The fabric, without having been steamed, is drawn over or in contact with a hot stationary surface, e.g. in a heated chamber such as chamber C described in BP 683,075 (J.S.D.C., 69 (1953) 105). C.O.C.

#### Spraying Liquids or Solids on to Paper, Cloth, etc.

Ilford

BP 828,469

The liquid or powder is sprayed on to one face of the web while air or other gas is blown toward the other face of the web so that, by resisting the passage of the sprayed material, it prevents the sprayed material from passing beyond the edges of the web. C.O.C.

#### Flocked Pile Fabric

Vertipile

USP 2,900,270

Individual clumps of wet fibres are placed on a base fabric coated with a thermosetting adhesive, so that the bottom of each clump is firmly secured to the adhesive. The fibres in each clump adhere to each other solely because they are wet and they are all recumbent. Flock is then deposited on the base so that it forms a pile in the areas surrounding the wet clumps. Any unsecured flock is removed and finally the adhesive is cured. C.O.C.

#### Bonded Fibre Fabric

Richard Haworth & Co (Manufacturing)

BP 824,941

A layer of non-felting thermoplastic fibres is pressed and while under pressure hot needles are inserted into it. This melts the fibres touched by the needles and causes them to adhere to other fibres. The mass is then allowed to cool before the pressure is released. C.O.C.

#### Bonded Fibre Fabric

United Plastic Industries

BP 787,073

BP 824,572

Powdered thermoplastic resin is impelled into an advancing layer of fibres by striking the powder with rapidly rotating impelling surfaces, the particles so impelled being directed into the fibre layer by a current of air. The impregnated material is then heated, compressed, and cooled. Suitable apparatus is described. C.O.C.

#### Metallising Cellulose Acetate Articles

Société des Usines Chimiques Rhône-Poulenc

BP 828,770

Incorporation of  $< 2\%$  of an elastomer containing urethane, urea, and amide linkages, e.g. Vulcaprene AC, gives cellulose acetate good adhesive power for metal coatings. C.O.C.

#### Preventing Beaded Edges when Coating Webs (I p. 305)

Antistatic Finish for Textiles (III p. 307)

Thermofixation Effect on Wool (VI p. 320)

Leather Substitute (XIII p. 329)

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

#### Increased Retention of Titanium Dioxide (C.I. Pigment White 6) and other Fillers used in Paper-making by the Action of Sodium Aluminate

G. Rieck and O. Huber

*Das Papier*, 13 (1959) 439-442

*Chem. Abs.*, 53 (25 Nov 1959) 22941

Retention of fillers, especially  $\text{TiO}_2$ , is greatly increased by adding Na aluminate which also improves the clarification of the white water. Sheet properties, e.g. brightness, opacity, and absorptivity, were also improved. C.O.C.

### The Z-Orientation in Paper

E. A. Aalto

*Seensk Papperstidning*, 63 (15 Feb 1960) 58-61 (in English)

In sheet formation some fibres will not be completely parallel to the *xy*-plane (parallel to the wire), but will have a dimensional component in the *Z*-direction, normal to the sheet. *Z*-orientation increases with increasing basis weight since the chance that a fibre will deviate from the *xy*-direction must depend on the ratio of the average fibre length to sheet thickness. It is suggested that the first layer deposited during sheet-making is highly plane-orientated, the amount of *Z*-orientation increasing with increasing distance from the wire. The small but distinct increase of *Z*-orientation with increased drainage time is explained by the greater pressure against the fibre mat at high drainage rates forcing the fibres into a horizontal position. This is confirmed by the fact that density decreases slightly with increasing drainage times. *Z*-orientation also decreases slightly with increased wet pressures and with increased heating times which may be due to increased *xy*-orientation or to fibre deformation. Delamination force is controlled by fibre-to-fibre bonding as well as by *Z*-orientation. R.A.

### Alkaline Solutions of Cellulose with Special Reference to Cupriethylenediamine Solutions

H. Vink *Seensk Papperstidning*, 63 (31 Jan 1960) 24-27 (in English)

Direct solvents for cellulose fall into three groups, i.e. conc. acids, conc. salt soln. and alkaline soln. containing bulky and complex-forming cations. Acids and salt soln. present inadequate solvating power and/or severe degradation. In the third group pure alkali soln. are relatively unimportant as they, too, possess limited solvating power and are not easily attainable. The only important solvents are, therefore, complex-forming alkali soln. and in particular cupriethylenediamine soln. 25 references. R.A.

### Heat Transfer during Yankee Drying

L. Jansson-Herminge

*Seensk Papperstidning*, 63 (31 Jan 1960) 15-23

Experiments carried out at the Swedish Central Laboratory have resulted in the development of equations showing the influence of physical factors on drying. The dependence of rate of evaporation on thickness, thermal conductivity, and ventilation is discussed and the results of experimental determination of heat transfer capacity of paper and its dependency on porosity are presented. When dimensioning a yankee cylinder account must be taken of the interaction between the mantle and cylinder. An equation gives the amount of water per time and surface area which can be taken up by the ventilation air at various partial pressures of the water vapour in the air and in the web and at various conditions of blowing the air against the web. Graphs show heat transfer as a function of porosity, rate of evaporation as a function of web temp. of the dew point of the air, and of the temp. of the ventilating air; and the connection between web temp. and ventilation air dew point. R.A.

### Fading of Azo Dyes in Cellulose Acetate Film

Y. Ishii and S. Uchida

*Senohoku to Kako*, 3 (1957) 191-6*Chem. Abs.*, 54 (25 Jan 1960) 1856

Cellulose acetate film treated with *p*-aminoazobenzene was developed by phenol, resorcinol, salicylic acid, 2-naphthol, 2-naphthylamine, and 2-hydroxy naphthoic acid respectively. The light absorption spectra of the dyed films were obtained and changes in the spectra on exposure to ultraviolet radiation discussed. Treatment with  $\text{CuSO}_4$  slightly changed the spectra of film developed with resorcinol or 2-naphthol but fading was much reduced. The maximum absorption of films developed with 2-naphthylamine increased on exposure. C.O.C.

### PATENTS

#### Ketene Dimer-Fatty Acid Blends for Sizing Paper

American Cyanamid Co.

USP 2,901,371

A blend of a hydrophobic water-insoluble ketene dimer with a small amount of a water-insoluble higher fatty acid is self-emulsifying. Used as a size for paper it is chemically bound to the fibres and cannot be removed by vegetable or animal oils. C.O.C.

### Clear Glossy Non-blocking Coatings on Fibrous Substrates

Rohm &amp; Haas Co.

USP 2,901,453

An aqueous dispersion of (a) a water-insoluble linear addition polymer of  $\text{Ti}$  > 30% (Ti is that at 300 kg./sq.cm. determined by the method described by Williamson, *British Plastics*, 23 (Sept 1950) 87-90) and (b) salts of a linear copolymer of maleic anhydride and  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$  in equimolecular ratio and of mol.wt. 500-5,000, is used. Their application requires neither heat nor a catalyst. C.O.C.

Spraying Liquids or Solids on to Paper, Cloth, etc. (X p. 327)

Metallising Cellulose Acetate Articles (X p. 327)

Kappa Number—An International Measure of Degree of Delignification (XIV p. 331)

Kappa Number of Pulp. SCAN-CL59. Identical with ICCA-159 (XIV p. 331)

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

### Myrobalans (Cl. Natural Brown 6)—an Important Tanning Material

D. E. Hathway

*Trop. Sci.*, 1 (1959) 85-106

### Mechanism of Salt Stippen Formation and Suggested Methods of Control

J. J. Tancous and F. O'Flaherty

*J. Amer. Leather Chem. Assoc.*, 55 (Feb 1960) 66-78

An investigation of the grain defect known as salt stippen. Histological studies revealed that stippen results in rupture of the grain tissues of the hide and that it develops initially during curing and that bacteria are secondarily involved. Spectrographic and chemical analyses showed that salt stippen begins as magnesium ammonium phosphate, that after liming it becomes a double salt by adding  $\text{CaCO}_3$  to its structure, and that after pickling and chrome tanning it exists as  $\text{CaSO}_4$ . Suggested methods of control include avoiding presence of Mg in curing salt, avoiding breakdown of hide tissues before and during cure, and preventing dehydration of hides while in store. C.O.C.

### The Different Effects of the Sorption of Calcium and of Sodium Ions on the Swelling of Hide Collagens

E. F. Mellon, H. A. Gruber, and S. J. Viola

*J. Amer. Leather Chem. Assoc.*, 55 (Feb 1960) 79-92

Swelling of hide collagen and absorption of Ca and Na ions by the collagen reach equilibria in very short time intervals. Therefore, these phenomena can be measured before secondary changes occur in the collagen. Quantitative measurements of the Ca and Na absorbed indicate that Ca ions are more firmly bound than Na ions and that absorption of Ca ions is limited while Na ions appear to be absorbed in the multilayer water of hydration. The concentration of Na ions in this bound water appears to be closely related to the concentration of Na ions in the surrounding solution. Increasing the salts present in the multilayer bound water increases the degree of swelling. The Ca ions bound on specific sites do not have much effect on swelling in these solutions containing Na ions. C.O.C.

### Production and Dyeing of Suede Leather

H. Wicki

*Kozvarati*, 8 (1958) 215-6*J. Amer. Leather Chem. Assoc.*, 55 (Feb 1960) 117

Suede leather retanned with vegetable tannins or diacydiamide resins cannot be dyed successfully in deep colours. Retanning with Cr, Cr-Al, or perhaps Cr-Zr is advised. Unpickled pelt, at pH 6-5, is tanned for 45-60 min. in 70% float containing  $\text{K}_2\text{Cr}_2\text{O}_7$  equal to 2%  $\text{Cr}_2\text{O}_3$  on the wt. of pelt. The slightly swollen skins are transferred to a second bath containing 2%  $\text{Cr}_2\text{O}_3$ , 42-50% basic, in 70% float and 0.3-0.5% of a cationic detergent which may be mixed with sperm oil. The bath is nearly exhausted in 2 hr. Then water is added to make 150% float and the skins swell slightly. This gives a full readily-dyed leather. The sooner the detergent is added, the better the results. Quaternary ammonium salts, containing the minimum of fatty components, are suitable cationic detergents. Cationic fat liquors are preferred because the resulting leather can easily be buffed. If skins for suede leather are sorted out after Cr tanning, a



Cr-Al retannage with addition of the cationic detergent is necessary. A suede with a nap that holds finger marks is obtained by a full fat liquor before the first drying. Cr soaps formed on the surface of the fibres give them the required sheen. Leathers fat liquored before and partly after drying are less brilliant. Anionic wax emulsions stable at pH > 7.5 give good results. Dyeing of suede may be compared to column chromatography of the dyes used. To obtain pastel dyeings the leather must be at pH 6.5 throughout its whole thickness. Striking through depends on the liquor ratio used; a dye which strikes through in a liquor ratio of 8:1 dyes only the surface in a 12:1 liquor. The best way to get deep colours is to dye first with 3-4% dye, liquor ratio 2:1. Practically all the liquor is absorbed and the dye is struck through. The 8% dye in a 20:1 liquor is added and this additional dye is fixed in about  $\frac{1}{4}$  of the leather thickness which is advantageous for buffing. This gives 10-20% better utilisation of the dye. 2:1 Cr-complex dyes give deeper colours than the 1:1 complex dyes but offer difficulties with respect to strike through. Spraying pigments on suede is not a suitable method of evening up colour; it is better to pair the skins flesh to flesh and stake lightly. Black suede, however, can be sprayed with aniline black pigments containing very little binder. Retannage with Cr alum can be replaced by a 1:2 mixture of Cr and Al alums which results in a more intense colour of better fastness to light. C.O.C.

## PATENT

#### Compositions for Removing Hair or Wool from Skins

H. Booth *BP 828,686*  
A mixture of a lime-free, water-soluble alkali, a little of a water-soluble sulphide, an antioxidant for the sulphide, and an oxidation promoter for the sulphide is used. The inhibitor must be able to diffuse with the sulphide through the skin and so be active at the hair root while the promoter must be incapable of diffusing through the skin and so only be active on the surface hair. Thus a "paint" to be used on sheepskins where the wool is to be dried without washing is made up of 100% NaOH (1.2 lb.), 60% Na<sub>2</sub>S (3-16 oz.), 100% Na<sub>2</sub>S (1.4 oz.), China clay (4.6 lb.) and water (1 gall.). C.O.C.

### XIII—RUBBER; RESINS; PLASTICS

#### Anionic Copolymerisation—Inability of Poly-(Methyl Methacrylate) Anion to Initiate Polymerisation of Styrene

R. K. Graham, D. L. Dunkelberger, and W. E. Goode  
*J. Amer. Chem. Soc.*, **82** (20 Jan 1960) 400-403  
By using 9-fluorenyllithium as initiator in anionic copolymerisation of styrene and methyl methacrylate it is shown that no styrene is present in the polymer. The 9-fluorenyl anion reacts only with methyl methacrylate, the resultant poly-(methyl methacrylate) anion is insufficiently basic to initiate polymerisation of styrene. Concluded from the above, for anionic copolymerisation of probably all systems where monomers differ greatly in polarity, that the nature of the anionic species, both initiating and propagating, is highly important. F.J.

#### Dye-sensitised Photopolymerisation of Vinyl Compounds. III—Polymerisation of Styrene by Cyanine Dyes

A. Watanabe  
*Bull. Chem. Soc. Japan*, **32** (June 1959) 557-564

#### Epoxide Resins; a Literature Survey

B. I. Buck *Brit. Plastics*, **32** (1959) 475-7  
*Chem. Abs.*, **54** (28 Jan 1960) 1893

Review, numerous references. C.O.C.

#### The State of Congo Red Molecules Sorbed in PVA Film

K. Fujino and F. Fujimoto  
**I—Creep Behaviour**  
*J. Soc. Textile Cellulose Ind. Japan*, **15** (May 1959) 414-417

At low dye concentrations the friction between PVA polymer chains is decreased, but increases at high concentrations. The recovery behaviour follows a similar pattern. From this it is concluded that the dye molecules form a network within the film.

#### II—Temperature Dependency of the Dynamic Properties of the Film

*Ibid.*, 418-421

Viscoelastic properties are measured by the vibrating reed method. Temperature dependencies of the mechanical loss tangent and real part of complex dynamic modulus are shown graphically. No crystallisation occurred during the heat treatment but the mechanical properties changed. It is concluded that the dye molecules associate. L.P.

#### Dry Colouring Polypropylene

R. A. Charvat *Modern Plastics*, **37** (3) (1959) 119-122, 124  
*Chem. Abs.*, **54** (25 Jan 1960) 1918

Pigments are more effectively dispersed in polypropylene by using a spherical venturi plate and hot cut pellets. C.O.C.

#### Processing Errors in Colouring Injection Moulded Products

K. Heinle and D. Hayer *Kunststoffe*, **49** (1959) 576-582  
*Chem. Abs.*, **54** (25 Jan 1960) 1919  
Faults in colouring injection moulded products, e.g. rough surface, silver streaks, localised colour concentration, "schlieren", differences in hue, and blooming are illustrated by colour photographs of test panels. Causes are moisture, excess of pigment, overheating, and insufficient mixing, distribution, and dispersion. C.O.C.

## PATENTS

#### Catalysts for Thermosetting Resinous Condensates

Catalin *BP 824,251*  
A mixture of boron oxide or a boric ester with organic compounds containing > 1 OH, COOH or CO group, e.g. glycerol and lactic acid, is a good catalyst for the polymerisation of thermosetting resins particularly those containing methylol groups. C.O.C.

#### Polyvinyl Resin Floor and Wall Coverings

Hardman & Holden *BP 824,339*  
Polyvinyl resin compositions to be processed in machinery normally used for linseed oil linoleum compositions consist of a thermoplastic polyvinyl or polyvinylidene resin binder containing an alkoxy or phenoxy aluminium acylate, alkoxy or phenoxy hydroxy aluminium acylate, oxo-aluminium acylate or a condensate of one of these compounds. C.O.C.

#### Fluorescent Foils

Gv *BP 828,831*  
Foil of polymeric synthetic materials are given vivid fluorescence by incorporation of 0.1-1.0% of a fluorescent brightening agent and 0.001-0.5% of a water-insoluble non-fluorescent colorant. The fluorescence makes the colour more visible and deeper in hue. Thus incorporation of  $\beta$ -copper phthalocyanine (C.I. Pigment Blue 15) and 4-(1',2',4,5-naphtho)-1,2,3-triazolyl-(2)-stilbene-2-sulphonic acid phenol ester gives plasticised polyvinyl chloride a strong blue fluorescence. C.O.C.

#### Coating Fluorinated Polymer Surfaces to make them Readily Wetted by Inks

Minnesota Mining & Manufacturing Co. *USP 2,808,229*

Fluorocarbon polymer surfaces are rendered readily wettable by inks, resins, and adhesives, without any deterioration, if they are heated to < 150°C. and the hot surface treated, in presence of moisture, with a volatile, readily hydrolysed, silicon, titanium or germanium compound, e.g. TiCl<sub>4</sub>. C.O.C.

#### Coating Polyfluoroethylenes with Metals

DuP *USP 2,808,228*

Polyfluoroethylene treated with a solution of an alkali metal, e.g. Na, in liquid NH<sub>3</sub>, is extremely adhesive to metals and colloidal metals deposited on it from them, form strongly adherent films. The NH<sub>3</sub> can be replaced by other non-metallic solvents capable of wetting the polymer. C.O.C.

#### Leather Substitute

DuP *BP 824,476*

A base of matted fibres bound together with an extensible polymeric binder is coated with an extensible, abrasion-resistant polymeric material. This coating is then perforated to render the composite material permeable to water vapour. C.O.C.

- Light Stabiliser for Halogeno Resins (III p. 307)  
Recent Developments in Polyurethanes (V p. 319)  
2-Cyanoethyl-*NNN'*-tetramethyldiamido-phosphate for rendering Acrylonitrile Polymers Flame Resistant (VI p. 321)

#### XIV—ANALYSIS; TESTING; APPARATUS

##### Measurement of Surface Tension based on Rate of Formation of New Surfaces

K. Berneis and R. Signer

*Helv. Chim. Acta*, **43** (1 Feb 1960) 232–235

From the rate of flow of a short liquid column in a slightly inclined capillary it is shown how the difference in surface tension at the two ends of the column may be determined by its relation to the rate of formation of new liquid surfaces. Data are given for toluene, 10% aq. ethyl alcohol, nitrobenzene (I), and I after addition of 0.06% and 0.33% by weight of water respectively. H.H.H.

##### Determination of Calcium and Magnesium with (Ethylenedinitrilo) tetraacetic acid—Studies in Accuracy

L. L. Lewis and L. M. Melnick

*Anal. Chem.*, **32** (Jan 1960) 38

By careful examination of the accepted procedures, sources of error are found to be due to: the colours of the indicators at the stoichiometric end point; the slowness of the magnesium-E.D.T.A. reaction; coprecipitation with the magnesium hydroxide at pH 12.5. P.B.S.

##### Detection of Albumen in Sizes and Finishing Materials—Albuminous Residues on the Fibre

A. Agster

*Textil Praxis*, **15** (Feb 1960) 168–171

The xanthoprotein, biuret, and ninhydrin reactions, the Millons reagent, and dyeing with acid dyes, are experimentally reviewed. Meroff's chloramine-benzidine blue reaction (cf. *Melliand Textilber.*, **37** (1956) 1304) is then described in detail and recommended as the best method extant for detection of albumen on the fibre. The accuracy is 0.01%, and although the reaction is essentially qualitative, it may be used under special conditions for quantitative estimations. This test is also useful in paper chromatography. H.H.H.

##### Electrophoresis of Dyes in the Gelatin Layer of Photographic Films

A. Sheludko, G. Konstantinov, and K. Tsvetanov

*Kolloid. zhur.*, **21** (Nov-Dec 1959) 747–753

The gelatin layer of photographic films freed from photosensitive substances is a suitable medium for the zonal electrophoresis of dyes. The electrophorograms show distinct separation. Optimal conditions for this type of electrophoresis are established. No relationship exists between electrophoretic mobility on paper and in gelatin. T.Z.W.

##### Determination of Red Dyes of the Naphthionic Acid Group

C. Dorlet

*J. pharm. Belg.*, **14** (1959) 227–231

*Chem. Abs.*, **54** (25 Jan 1960) 1853

Chemical and chromatographic methods give valuable results when determining the red dyes Ponceau 2R (C.I. 16150), disodium 1-(4-sulphonaphthylazo)-2-naphthol-5-sulphonate and trisodium 1-(4-sulpho-1-naphthylazo)-2-naphthol-4,6-disulphonate. They can be determined polarographically by placing the sample (1 ml. of 0.1% soln.) in the thermostat cell of the polarograph and adding a buffer (20 ml.), varying the difference in potential between the electrodes from 0–800 mv., fixing at 25° and passing N through for 10 min. before taking measurements. Values of  $E/2$  for the three dyes are 0.432, 0.324, and 0.368 respectively. The buffer consists of 0.1 M-citric acid (8.82 ml.), 0.2 M- $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  (to bring to 50 ml.) and gelatin (5 mg. %). Crystallisation of the dyes from  $\text{H}_2\text{SO}_4$  is described. C.O.C.

##### Paper Chromatography of 1,4-Bis(*m*-aminophenyl-sulphonamido)benzene and Related Azo Dyes

Z. Madeja-Kotkowska and J. Mastowska

*Zeszyty Nauk. Univ. Lodz.*, ser. II **5** (1959) 175–180  
1,4-(*m*- $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NH}_2$ ) $_2$   $\text{C}_6\text{H}_4$  (I) prepared by Chrzasczewska (*Chem. Abs.*, **50** (1956) 5294) proved to be chromatographically impure as did azo dyes prepared by coupling it with 2,6-HO( $\text{SO}_2\text{H}$ ) $_2$  or 1,3,7-HO( $\text{SO}_2\text{H}$ )( $\text{H}_2\text{N}$ ) $_3$ . Pure I prepared by double crystallisation of

its hydrochloride from alcohol, yielded a single spot,  $R_f$  0.47, with butanol:acetic acid:water (50:15:35 by vol.). The chromatogram was developed by coupling with 2-naphthol. A reddish yellow dye obtained by coupling with naphthionic acid had  $R_f$  0.38 when chromatographed as above. C.O.C.

##### Chromatography of Dye Intermediates. X—Paper Chromatographic Separation of the Hydroxy- and Amino-derivatives of Naphthalene

J. Latinák

*Collection Czechoslov. Chem. Commun.*, **24** (1959) 2939–2947 (in German)

*Chem. Abs.*, **54** (10 Jan 1960) 901

Separation and identification of 1- and 2-naphthol, 1,1'- and 2,2'-binaphthol, 1-iodo-2-naphthol, 1,3-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6-, and 2,7-dihydroxynaphthalene, 1- and 2-naphthylamine, 1,5- and 1,8-diaminonaphthalene, and 1,6- and 1,7-aminonaphthol is described using descending chromatography on Whatman No. 4 paper impregnated with  $\text{HCONH}_2$  and with 8:2 benzene-ethylacetate, 8:2-chloroform-ethylacetate, chloroform, carbon tetrachloride and cyclohexane, respectively as developers (in each case the developer being saturated with  $\text{HCONH}_2$ ). C.O.C.

##### Paper Chromatographic Separation of Direct Dyes

J. Kolšek

*Chemiker-Ztg.*, **83** (1959) 478–482

*Chem. Abs.*, **53** (25 Nov 1959) 22960

Separation can be effected by use of suitable solvents containing pyridine. To make the dye adhere to the starting line, a hydrophobic paper (Ederot Paper No. 202, J. C. Binzer, Hatzfeld/Eder) impregnated with dimethyl phthalate was used. The eluent was 1:4 pyridine-water. The dyes were dissolved in water containing pyridine and placed on the starting line as an elongated spot.  $R_f$  values of the components of 50 commercial dyes are given. C.O.C.

##### Infrared Analysis of Dyes. I—Yellow Food Dyes

M. Suzuki, E. Nakamura, and Y. Nagase

*Yakugaku Zasshi*, **79** (1959) 1116–9

*Chem. Abs.*, **54** (25 Jan 1960) 1855

Naphthol Yellow S (C.I. Food Yellow 1) (I), Yellow AB (II), Yellow OB (III), Tartrazine (C.I. Food Yellow 4) (IV), Sunset Yellow FCF (C.I. Food Yellow 3) (V), Auramine (C.I. Basic Yellow 2) (VI) and Butter Yellow (VII) were examined using the KBr pellet method. Detection up to about 40  $\mu\text{g.}$  would be possible by use of their characteristic absorption bands. Thus determination of VI and of VI present in IV was made using absorption at 1008  $\text{cm}^{-1}$  as the key band for IV and at 945  $\text{cm}^{-1}$  for VI. Standard deviation of the result for each component in the mixture was calculated by Youden's method (*Chem. Abs.*, **42** (1948) 2694). The values were 1.39 for IV and 1.55 for VI. Keybands ( $\text{cm}^{-1}$ ) of these dyes are: I, 1050, 1017, 796; II 922, 748, 700; III 1109, 723; IV 1040, 1008, 775; V 1040, 990, 903; VI 1000, 960, 945; VII 928, 827, 767. C.O.C.

##### Separation and Identification of Food Dyes

A. C. Cooke

*New Zealand J. Sci.*, **2** (1959) 260–5

*Chem. Abs.*, **54** (25 Jan 1960) 1759

Thaler and Sommer's method (*Chem. Abs.*, **48** (1954) 714) is used with the alteration that the eluent is butanol: 95% alcohol:water (1:1:1). Colour, fluorescence, reaction with 10% NaOH and conc. HCl, and  $R_f$  values are given for 42 dyes. C.O.C.

##### Isolating Water-soluble Dyes from Foods

E. L. K. Dagneaux and A. J. Weide

*Chem. Weekblad.*, **54** (1958) 675

*Chem. Abs.*, **54** (25 Jan 1960) 1759

Thaler and Sommer's method (*Chem. Abs.*, **48** (1954) 4714) (extracting with water, dyeing on to wool yarn and eluting with ammonia) is improved by extracting the dry food with 5% ammonia in aqueous alcohol (70:30). Difficulties caused by presence of proteins are overcome by modifying the subsequent chromatographic technique, e.g. by making a mixed chromatogram with the expected dye. This expedient is usually needed only for products made from flour and not always for them. C.O.C.

##### Detection of *p*-Phenylenediamine in Hair Dyes

T. Brouwer

*Chem. Weekblad.*, **55** (1959) 325–7

*Chem. Abs.*, **53** (25 Nov 1959) 22755

A routine method for detecting *p*-phenylenediamine in presence of *p*-tolenylenediamine, 2,5-diaminobenzoic acid or other derivatives of *p*-phenylenediamine is based on the reaction

with vanillin and HCl followed by chromatographic separation of the coloured products. The indamine reaction is used as a preliminary test to eliminate samples not containing *p*-phenylenediamine or its derivatives. The ascending chromatograph is developed on Whatman No. 1 paper with the upper layer a 35:10:20 mixture of butanol, conc. HCl, and water. A solution of vanillin in ether is dropped on the paper and the position of the spots compared with that of pure *p*-phenylenediamine run simultaneously. Full working details are given.

C.O.C.

#### Rapid Test for Identification of Phenylenediamine Isomers

R. G. Frieser and P. A. Scardaville

*Anal. Chem.*, **32** (Feb 1960) 196

A distinctly different coloured precipitate is formed with each of the three phenylenediamines when their aqueous solutions are treated with phosphomolybdic acid reagent. The test can be carried out in a test tube, on a spot plate, or on spot test paper.

P.B.S.

#### Migration Distance in Paper-electrophoresis

K. Sakamoto, K. Saito, and A. Nagata

##### VII—Migration Distance of Dyes. 2

*Bull. Agr. Chem. Soc. Japan*, **28** (1959) 89-94

Migration distances of 31 dyes were measured using a horizontal-type paper electrophoretic apparatus permitting evaporation. 4 and 30% aqueous acetic acids were used as solvents. There was close relationship between the extent of osmotic flow of the dyes secured by evaporation of solvent and the displacement ratio defined as (displacement of the substance from its dropped position):(distance of the soaked up front of the acetic acid from the dropped position of the substance).

##### VIII—MG Values of Dyes

*Ibid.*, 95-9*Chem. Abs.*, **53** (25 Nov 1959) 21381

Dyes are classified in several groups on the basis provided by the data of displacement ratios. Their migration values, which are independent of the electric current, voltage, time for electrophoresis, dropped position or the length of the filter paper, are given.

C.O.C.

#### Identification of Remazol (FH) Dyes on the Fibre

A. Bode *Melliand Textilber.*, **40**, (Nov 1959) 1304-1305

If a dyed or printed sample is freed from surface dye by boiling for 10 min. in alkali-free detergent, and is then boiled for 3-4 min. successively in a 1:1 mixture of dimethylformamide and water, in dimethylformamide, and finally in a 1:1 mixture of alcohol and glacial acetic acid, only reactive dyes do not bleed. The phthalocyanine derivatives Procion Brilliant Blue H7GS (C.I. Reactive Blue 3) and Cibacron Turquoise Blue G (C.I. Reactive Blue 7) may bleed, but are identified by spotting with conc.  $\text{HNO}_3$ , when they turn green, and with  $\text{ZnCl}_2$  in HCl, when, unlike other phthalocyanine dyes, they turn reddish navy. On boiling another soaped sample of a reactive dyeing for 15 min. under reflux with 1 ml. conc.  $\text{H}_2\text{SO}_4$  per litre and 2 g.  $\text{Na}_2\text{SO}_4$  per litre in presence of white wool, this is coloured by all Procion and Cibacron dyes except the phthalocyanine blues, and by none of the Remazol dyes except for heavy dyeings of Remazol Black B. The latter is identified by spotting with conc.  $\text{HNO}_3$ , when it turns blue-green, whereas Procion Black HGS (C.I. Reactive Black 1) and Cibacron Black BG change to olive-brown.

S.M.J.

#### Analytical Densitometry for Colour Print Evaluation

J. W. Onley *J. Opt. Soc. Amer.*, **50** (Feb 1960) 177-182

For a wide gamut of dye combinations for a reflection print material, equivalent neutral densitometry compares favourably with colorimetric measurements for the evaluation of colour prints. Over a limited range of normal printing conditions there is a linear relationship between reflection density and distance from the illuminant point along the vectors of a colorimetric dye grid. Both neutral scale and picture-area densitometry offer advantages for the measurement of matched and rejected prints. It is necessary to bear in mind the possible limitations of neutral scale densitometry and to utilise picture area measurements for reproductions in which conditions vary considerably from "normal".

C.O.C.

#### Semi-micro Method of High Accuracy for Determining Sulphur in Wool

B. J. Myers *J. Textile Inst.*, **50** (Aug 1959) T 494-503

Conditions are described under which the perchloric-nitric acid oxidation procedure for determining the sulphur content of wool, gives highly reproducible and accurate results.

C.O.C.

#### Kappa Number—An International Measure of Degree of Delignification

P. O. Bethge and K. Wilson

*Svensk Papperstidning*, **63** (31 Jan 1960) 28-31

Summarising the development, method, principles, and practical applications of the method which has been adopted as the first inter-Scandinavian (SCAN C-1:59) and as an Australian (P 201m-59) method and is shortly expected to replace TAPPI T214:Permanganate Number of Pulp. A rule-of-thumb for converting Roe numbers to

$$\text{Kappa numbers is given as: Roe Number} = \frac{\text{Kappa Number}}{5.0}$$

$$\text{for spruce sulphite and Roe Number} = \frac{\text{Kappa Number}}{6.5}$$

for pine and spruce sulphate. These relationships are, however, not reversible and cannot be used for converting Kappa numbers to Roe numbers. The relationship with lignin content for sulphite and sulphate pulp is—

Kappa Number  $\times 0.13$  = Klason-lignin (%) and  
Kappa Number  $\times 0.17$  = Noll-lignin (%) for sulphite,  
Kappa Number  $\times 0.15$  = Noll-lignin (%) for sulphate,  
Kappa Number  $\times 0.16$  = Noll-lignin (%) for semi-chemical pulp.

R.A.

#### Kappa Number of Pulp. SCAN-CI:59. Identical with ICCA-1:59

*Svensk Papperstidning*, **63** (31 Jan 1960) 32-33*Norsk Skogindustri*, **13** (Dec 1959) 469-470

(in English)

This is the first of the inter-Scandinavian test methods. There will be four classes: C = Chemical and semichemical pulp, P = paper and paperboard, M = mechanical pulp, and N = non-fibrous materials. A conditioned sample is weighed to the nearest 0.001 g. of pulp which will consume approx. 50% of 0.1 N- $\text{KMnO}_4$ .  $\text{KMnO}_4$  consumption must be between 30 and 70%. The sample is disintegrated in 500 ml. dist.  $\text{H}_2\text{O}$  without extensive cutting of the fibres, transferred to a 1500 ml. beaker and placed in a constant temp. bath at  $25 \pm 1^\circ\text{C}$ . A mixture of 100 ml.  $\text{KMnO}_4$  and 100 ml. 4 N- $\text{H}_2\text{SO}_4$  is added at  $25^\circ\text{C}$ . and the soln. made up to 1,000 ml. After exactly 10 min. the reaction is terminated with 20 ml. 1.0 N-KI and immediately titrated for free iodine with 0.2 N-sodium thiosulphate using 0.2% starch as indicator. A blank is carried out without pulp. Kappa Number =  $ad/m$  where  $a$  =  $10(b-c)n$  ( $a$  =  $\text{KMnO}_4$  consumption in ml.,  $b$  = thiosulphate consumption in ml. of blank,  $c$  = thiosulphate consumption in ml. of test,  $n$  = normality of thiosulphate,  $d$  = factor for correction to 50%  $\text{KMnO}_4$  consumption dependent on value of  $a$ ,  $m$  = weight of oven-dry sample).

R.A.

#### Determination of Sulphates in Dyes

C. Kotakis and E. Kokoti-Kotaki

*Chim. Chronika*, (Athens, Greece) **24** (1959) 114-7

Dyes containing sulphonic groups in the molecule form complexes with *p*-toluidine hydrochloride which permit removal of the dye by filtration of the complex and further extraction with amyl alcohol. The sulphates are then determined by precipitation with benidine hydrochloride.

C.O.C.

#### DIN 1959 54 031. Testing of Dyed and Printed Textiles for Colour Fastness to Soda Boiling

Replaces DIN 53 984.

C.O.C.

#### DIN 1959 54 032. Determination of the Colour Fastness of Dyed and Printed Textiles to Alkali

Replaces DIN 53 965.

C.O.C.

#### DIN 1959 54 038. Testing of Dyed and Printed Textiles for Colour Fastness to Stoving

Replaces DIN 53 972.

C.O.C.

#### DIN 1959 54 039. Determination of the Colour Fastness of Dyed Textiles to Mercerising

Replaces DIN 53 968.

C.O.C.

#### DIN 1959 54 044. Determination of the Colour Fastness of Dyed and Printed Textiles to Carbonising with Aluminium Chloride

A new German standard.

C.O.C.



**DIN 1959 54 054. Determination of the Colour Fastness of Dyed and Printed Textiles to Decatizing**  
Replaces DIN 53 975. C.O.C.

**New Artificial Weathering Methods for Rubber, Plastics and Textiles**  
G. F. Bush

*Amer. Dyestuff Rep.*,  
49 (8 Feb 1960) 33-39 (64-70)

Review of the problems and progress (including some new data from the author), mainly since 1955, on the artificial weathering of materials. 77 references. C.O.C.

**Fastness to Ironing of Azoic Dyeings on Cotton**

W. Kirst *Textil Praxis*, 15 (March 1960) 290-301

Test procedure was based on the standard specification DIN 54 022 of the German Commission for Fastness in Textiles which is generally in agreement with the methods approved by the European Commission for Fastness in Textiles. Altogether 39 fast bases or salts combined with 20 azoic coupling components were tested at 190-280° C. About 41-5% of the dyeings showed reversible colour change when ironed at 190° C. At appreciably higher temp. of pressing the proportion of dyeings showing permanent colour change increased. Fastness to ironing is affected by treatments before dyeing (bleaching, mercerising), after-soaping, and even the R.H. at which tests are carried out. There are 7 tables of test results. L.A.T.

**New Developments in Evaluating "Wash-and-Wear" Performance**

J. R. Berceaw *Amer. Dyestuff Rep.*,  
49 (22 Feb 1960) 37-43 (111-117)

The "built-in wash-and-wear" performance of fabrics of blends of hydrophobic thermoplastic fibres and cotton is now so widely accepted that further advances must come through subtle, incremental improvements in blends, construction and finish or by introduction of a new fibre. Incremental improvements can be obtained, e.g. by replacing cotton by rayon in blends with polyester fibre. Such improvements require investigation of numerous variables and need more precise methods for assessing progress. Because of this techniques have been developed for making and testing optimum small-scale fabric samples, which reliably predict "wash-and-wear" performance of their commercial analogues. A more fundamental problem, that of objectively measuring fabric wrinkles, has been solved by a new application of an established principle involving low-angle light projection. High-intensity light directed through a slit into a cloth gives an exaggerated contour line of the fabric surface. This line can be analysed manually or electronically to give an index of fabric wrinkling which is in excellent accord with subjective evaluations. In addition it has other uses, e.g. to determine the ability of coloration and surface texture to mask fabric wrinkles. C.O.C.

**Location of Areas of Reaction in Chemically Treated Cotton Cellulose**

V. W. Tripp, A. T. Moore, I. V. de Gruy, and M. L. Rollins  
*Text. Research J.*, 30 (Feb 1960) 140-147

The modification of cotton cellulose by various treatments normally occurs at submicroscopic levels. Observations with the electron microscope has been useful in showing regions of the fibre affected by various treatments, including dyeing, mercerisation, acid and enzymatic hydrolysis, derivative formation, and resin impregnation. The appearance of fibre fragments treated in these ways or derived from treated fibres is illustrated and discussed. P.G.M.

**Identification of Textile Coatings by Infrared Spectroscopy**

F. H. Forziati, R. T. Hite, and M. K. Wharton  
*Amer. Dyestuff Rep.*, 49 (22 Feb 1960) 29-33 (103-107)

A method suitable for the qualitative analysis of very small specimens consists of a series of extractions which separate the specimen into a number of fractions which are identified by infrared spectroscopy. It yields rapid and positive identification of most components of textile coatings. However some inorganic pigments have no infrared absorption and other methods of identification have to be used for them. C.O.C.

**The Tearing Strength of Fabrics. I—Review of the Literature**

P. W. Harrison *J. Textile Inst.*, 51 (March 1960) T 91-T 131  
A comprehensive and critical survey, 211 references. C.O.C.

**Determination of Amines causing Resin-finishes to Smell**

R. Amishänslin *Textil-Rund.*, 15 (March 1960) 122-125

A refinement of the test suggested by Kraus in 1950. The Kraus test permits neither determination of primary amines nor ready differentiation between secondary and tertiary amines. In addition ammonia interferes with the test. The new method is: 6 g. of the material cut into small pieces are put together with 50 ml. of distilled water into a flask. 1 g. silver oxide to oxidise free formaldehyde and 1 g. soda calc. to liberate the amine from the salts are added. 5 ml. 5% (vol.) acetic acid are filled into the receiver which is cooled with ice. After boiling has started distillation is carried out for 5 min. so that 3-5 ml. distil over. Spot test: A number of spots are produced on filter paper by applying about 1 mm.<sup>3</sup> of the distillate every time. Presence of primary and secondary amines can be detected by spraying the spots with ninhydrin reagent and with a freshly prepared solution of acetaldehyde-sodium-nitroprusside respectively. Tertiary amines can be detected with the aid of phosphotungstic acid and stannochloride in HCl. Application of paper chromatography allows individual identification of the amines. W.M.

**Consumers' Reaction to "Wash-and-Wear"**

G. M. Smith *Amer. Dyestuff Rep.*,  
49 (25 Jan 1960) 43-46 (P 44-P 47)

Complaints and comments received from consumers are listed with particular reference to garments made from fabrics treated to give "wash-and-wear" properties. P.G.M.

**Solubility of Wool in Potassium Thioglycollate**  
H. G. Fröhlich

*S.V.F. Fachorgan*, 15 (March 1960) 198-202

This new test for the assessment of the degree of modification of wool as a result of varying chemical treatments was first described by F. G. Lennox (*Text. Research J.*, 28 (1958) 949). 0.5 g. of wool is treated in 50 ml. of freshly prepared 0.1 N-HS-CH<sub>2</sub>COOK soln. at 50° C. for 60 min. The percentage loss in weight of the material, known as the Thioglycollate Number, is a useful index in assessing wool damage. Its average value for untreated wool is about 16. Results of comparative tests on acid and alkali damaged wool are shown in tables and graphs. L.A.T.

PATENT

**Laboratory Dyeing Machine**

H. Horsfall *USP* 2,901,902

A vertical support able to move up and down carries yarn holders arranged around it so that as it moves so do the samples of yarn in the individual dyebaths. C.O.C.

Tartrazine (C.I. Food Yellow 4) B.S. 3211:1960 (IV p. 308)

Specific Colour Reaction of Rutin (C.I. 75730) and Differentiation from its Analogues (IV p. 312)

The Solubility of Wool Dyes—Its Assessment and Practical Significance (VIII p. 323)

Air-permeable PVC Coated Fabric for Upholstered Furniture. BS 3217:1960 (X p. 326)

The Z-Orientation in Paper (XI p. 328)

XV—MISCELLANEOUS

**Teamwork in the Dye House**

R. Regimbal *Canadian Textile J.*, 77 (3) (5 Feb 1960) 21-4

A discussion of the broad concept of teamwork in industry with an analysis of its close relationship to human relations. C.O.C.

**Work Study in Dye Houses**

G. C. Battye *Text. Manuf.*, 86 (Feb 1960) 75, 76

**Ammonium Benzoate as an Atmospheric Corrosion Inhibitor for Metal Surfaces**

S. A. Gintsburg

*Zhur. priklad. khim.*, 33 (Jan 1960) 243-246

Steel, brass, and nickel plated samples were wrapped in paper impregnated with various solutions of ammonium benzoate and exposed to a humid atmosphere. Ammonium benzoate was found to be 25-30 times as effective as sodium benzoate (commonly used as inhibitor) for protecting steel and iron. L.S.L.



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The Society of Dyers and Colourists

## ADVANCE ANNOUNCEMENT

### Standard Methods for the Determination of the Colour Fastness of Textiles

The methods of fastness testing sponsored by the Society of Dyers and Colourists are published as a separate handbook under the title "Standard Methods for the Determination of the Colour Fastness of Textiles", the first edition appearing in 1955.

Developments in fastness testing, particularly internationally, necessitated the publication in 1958 of a supplement to the handbook and since then further developments have occurred. **Instead of issuing a second supplement, however, the Society's Fastness Tests Co-ordinating Committee decided that it would be more convenient for the Society to issue a Second Edition of Standard Methods for the Determination of the Colour Fastness of Textiles** which will shortly be available from the offices of the Society.

The Second Edition contains the tests, etc., which appeared in the *Journal* as Sponsored Publications since the supplement was published—

Light: Daylight at High Humidity

The use of fading lamps

Pleating and Setting

and also three tests which are now appearing for the first time—

Light: Daylight (U.S.A. Method)

Xenon lamp

Vulcanising: Hot air

Mainly in the interest of international agreement two of the original tests have been substantially modified: these are—

Burnt-gas fumes

Perspiration

whilst minor modifications have been made to certain others.

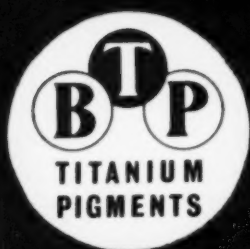
Many of the tests in the handbook have become Recommendations of the International Organisation for Standardisation and have been adopted as National Standards in many countries including the United Kingdom. A list of equivalent national standards is included in each test which should be of value where exports and imports are concerned.

To facilitate ease of reference, the tests have now been arranged alphabetically and a standard lay-out has been adopted.

**THIS HANDBOOK IS UNDOUBTEDLY THE MOST COMPREHENSIVE AND UP-TO-DATE SOURCE OF INFORMATION ON COLOUR FASTNESS TESTING IN THE WORLD AND IS INDISPENSABLE WHEREVER COLOUR FASTNESS TESTS ARE MADE.**

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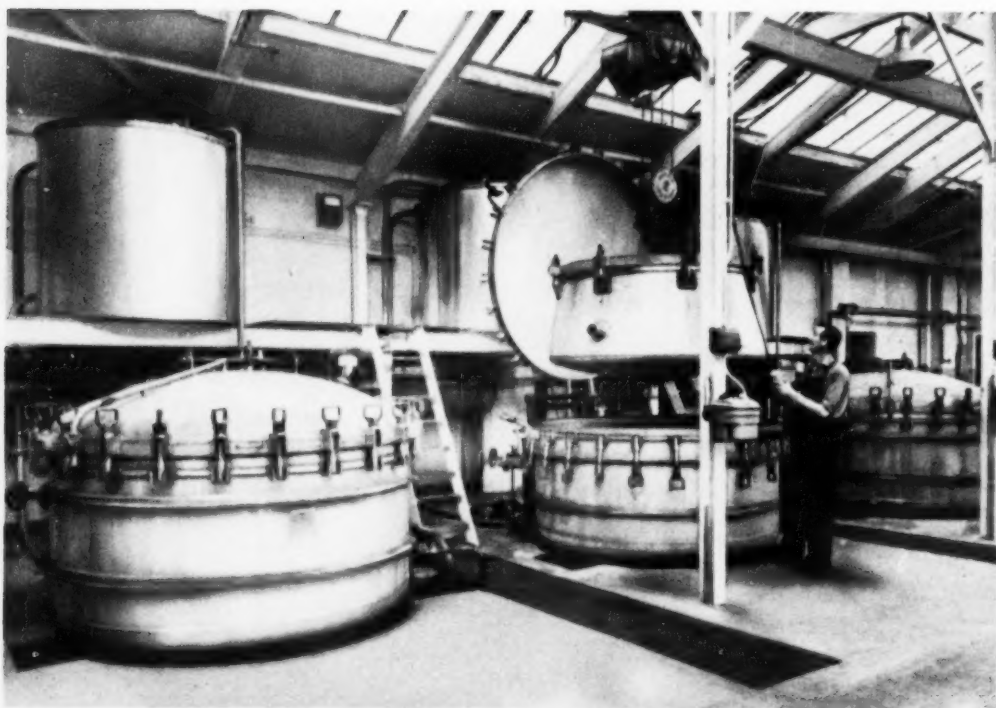
## High Temperature Dyeing

Amongst our wide range of Dyeing Plant are machines for natural or synthetic loose materials, slubbing, yarn in all forms and piece goods.

The High Temperature machines are designed for operation at temperatures up to and above 130°C.

The illustration shows an installation of Longclose Conical Pan High Temperature Loose Material Dyeing Machines, each with a capacity up to 800 lb. depending on the material to be dyed.

*Fully descriptive literature sent on request.*



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## APPOINTMENTS

Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, and MISCELLANEOUS ITEMS are invited for insertion on this page. Advertisements of Appointments Wanted are gratis to members, but must not exceed twenty-four words.

All inquiries relating to Advertisements should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS and COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS and COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

### APPOINTMENTS VACANT

#### AUSTRALIA

A leading Australian Textile Manufacturing Company with over 3,000 employees, engaged in Spinning, Weaving, Dyeing and Finishing, requires the services of the following senior Executives—

##### CHIEF CHEMIST

**Duties**—To be responsible for the efficient administration and co-ordination of the Chemical and Physical Testing Laboratories and Quality Control practices.

**Qualifications**—The applicant will need to have suitable academic qualifications, and must have a sound knowledge in the major fields of Textile testing, and preferably to have had practical experience in the industry and in the use of quality control techniques.

Preferred age—28 to 40 years.

##### DYEHOUSE MANAGER

**Duties**—To be responsible for the efficient administration and direction of all sections of the Dyeing and Finishing Plant which is engaged in the dyeing and finishing of natural and man-made fibre fabrics on Jigs, Winches and Pad-Rolls.

**Qualifications**—Applicants must have adequate secondary and tertiary education, proven managerial ability, and the necessary technical experience in the dyeing and finishing of such fabrics.

Preferred age—33 to 40 years.

▽

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A Contract based on a generous salary and superannuation is available to the successful applicants. Free passages to Australia and assistance with housing will be provided.

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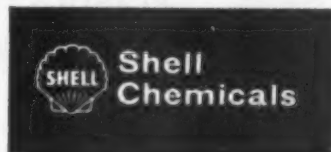
The positions offer interesting work and provide an opportunity for development with an old established and progressive Company.

##### Applications

Detailed written applications will be treated in strictest confidence and will be immediately acknowledged, and should be addressed to

Box V197

#### AUSTRALIA



##### TECHNICAL ASSISTANT

AN Assistant is required by the Detergents Sales Manager in the Manchester office of the Shell Chemical Company. Applicants for this position should not only have experience in the textile trade, but should also possess a technical qualification in this field. The successful candidate will be expected in due course to become an outside technical representative and there are good prospects for a successful career in an expanding company. Age preferably not over 26.

Salary according to age, qualifications and experience. Generous pension scheme and other benefits.

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SHELL CHEMICAL COMPANY LIMITED  
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170 Piccadilly, London W.1

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A suitable applicant will be offered a salary excellent by Canadian standards of approximately £37 weekly plus bonus, pension, sickness benefits, life insurance and removal and travelling expenses.

For an interview in Manchester early August write F. G. Reed, 104 Victoria, Magog, Province of Quebec, Canada, giving full details of education and experience.

**EXPERIENCED DYER** required by Leicester hank yarn dyeing firm. Applicants must be conversant with the application of all classes of fast dyes to wool, with some experience of other fibres. Willing to supervise evening shifts. Salary £200-£1,300 according to ability. Pension scheme. Assistance given if disturbance necessary. Box V199

##### CHIEF CHEMIST

JOHNSON & JOHNSON (Great Britain) LTD. invite applications for the above appointment in their Laboratories at Gargrave Yorkshire.

Duties will involve supervision and co-ordination of Research and Development activities, and of Quality Control, in connection with Surgical Dressings and Non-woven Fabrics.

Candidates should be well qualified in chemistry, and should have had previous experience in textiles, textile finishing and resin application. Technological skill should be combined with marked qualities of leadership, drive and organising ability.

An attractive salary, commensurate with qualifications and experience, will be paid. Future prospects are excellent.

Applications, in strict confidence, to Research Director, Johnson & Johnson (Great Britain) Ltd., Slough, Bucks.

##### IMPORTANT POSITION IN U.S.A.

##### DIRECTOR OF RESEARCH AND DEVELOPMENT IN DYESTUFFS AND RELATED PRODUCTS

WE are an extremely successful and expanding American producer of Azo Dyes. We are now seeking a chemist of stature for the post of DIRECTOR OF RESEARCH AND DEVELOPMENT.

The individual who will successfully fill the requirements for this position should be between 30 and 45 years of age. He shall have had various types of successful experience in research work, practical plant work and/or product development. He must be conversant with the newer trends in dyestuffs manufacture.

He should be able to lead and inspire a research group and also be a chemical specialist in his own right in any one of the various fields of work of current interest to our company.

The present interests of our company are in the following fields—

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This is a rare growth opportunity and the financial arrangements have been left open to attract the right man. The company will naturally undertake all necessary legal obligations and will attempt making entry, and working and living in the U.S. as comfortable as possible.

All replies will be dealt with personally by the President of the Company. Please write to E. C. Warshaw, President, Berkshire Color and Chemical Co., Delawanna, New Jersey, U.S.A.



# Shell Chemicals

## PLASTICS COLOURISTS VACANCIES

Petrochemicals Limited have the following vacancies—

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Applicants must have had several years' experience in the colouring of plastics and must be capable of supervising a team of Colourists.

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The vacancies are for shift work in the Plastics Colour Laboratory at Carrington. Applicants should preferably have experience in colour control and colour matching, although candidates with an aptitude for colour work will be considered for training to the required standard. These positions are all established and pensionable, and carry attractive salaries commensurate with experience and ability. Generous Contributory Pension Fund, excellent Cafeteria and Social and Sports Club facilities. Any 1960 holiday arrangements will be favourably considered.

Applications, bearing reference SDC/43, should be addressed to—

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**DYEHOUSE MANAGER**, aged 31, married, seeks responsible administrative, technical position in Australia. Qualified Bradford Institute Technology, London City and Guilds, dyeing and finishing all fibres. Box W627

**FULLY QUALIFIED DYER**, 25 years experience in dyeing and wet processing of hanks, package, slubbing and piece on wool and other fibres requires position. First-class references. Terminating contract abroad and available in England end July. Write P.O. Box 143, Uitenhage, C.P., South Africa.

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### College Diploma in Textile Manufacture

A three-year full-time course providing a broad basis of fundamental scientific principles in which a wide range of technical subjects is developed to a high standard. In the third year the student may specialise in Hosiery Manufacture or Warp Knitting.

### College Diploma in Dyeing and Finishing

A three-year full-time sandwich course. On successful completion of this course students may undertake a further year's study leading to—

### Higher National Diploma in Applied Chemistry (Dyeing)

For further details of the courses and entrance qualifications write to the Principal, Burton Street, Nottingham.

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Petch, K. E., formerly of "Islandbawn", Muckamore, Co. Antrim, Northern Ireland, to 5 McMaster Crescent, Castledawson, Co. Derry, Northern Ireland  
Redston, R. W., formerly of P.O. Box 120, Chateauguay Basin, Quebec, Canada, to c/o Hubbard Felt Co. Ltd., 425 Marien Avenue, Montreal East, Quebec, Canada  
Rigby, T. P., formerly of 38 Lynton Drive, Heaton, Bradford 9, Yorkshire, to 31 Canford Drive, Allerton, Bradford  
Rouse, J., formerly of "Ardgowan", 8 Ardgowan Street, Paisley, Scotland, to 62 Crow Road, Paisley, Scotland  
Seeley, C. W., formerly c/o The Barracks Fabrics Printing Co. Ltd., Lower Heys Mill, Macclesfield, Cheshire, to "Collinwood", Rainow Road, Macclesfield, Cheshire

Shah, N. H., formerly of Seth C. Girdhardas Road, near Govt. Housing Society, Navarangpura, Ellisbridge, Ahmedabad 6, India, to Near Govt. Housing Soc. No. 1-18, Navarangpura, Ahmedabad 9, India  
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Swarbrook, I., formerly of 14 Eversley Avenue, Leek, Staffordshire, to 45 Nab Hill Avenue, Leek, Staffordshire  
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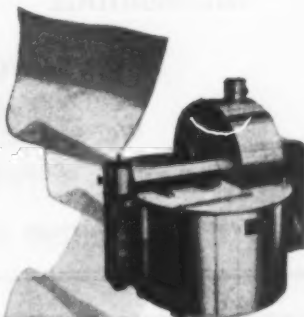
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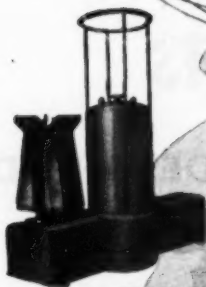
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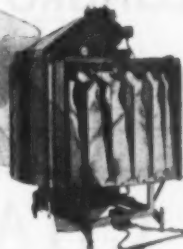
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For all types of nylon hose, half-hose including garments made from synthetic yarns.



Builders of dyeing machines for loose stock, hanks, packages, piece-goods, fabric and hose; also finishing machines for all classes of circular knitted and warp loom fabrics and garments. Pre-boarding and finishing machines for nylon hose.

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**ADVANCE ANNOUNCEMENT**

THE SOCIETY OF DYERS AND COLOURISTS

**THE SIXTH  
GEORGE DOUGLAS LECTURE**will be given at the **MIDLAND HOTEL BRADFORD**on **Thursday 13 October 1960**at **7.15 pm**by **A. B. D. CASSIE C.B.E M.A D.Sc F.Inst.P**  
(Director of Research Wool Industries Research Association)on ***Wool as a Fibre in  
Dyeing and Finishing***

Members of other societies  
and the public will be  
welcome at the lecture

An appeal is made for full support of this  
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friends. All interested are invited to attend.

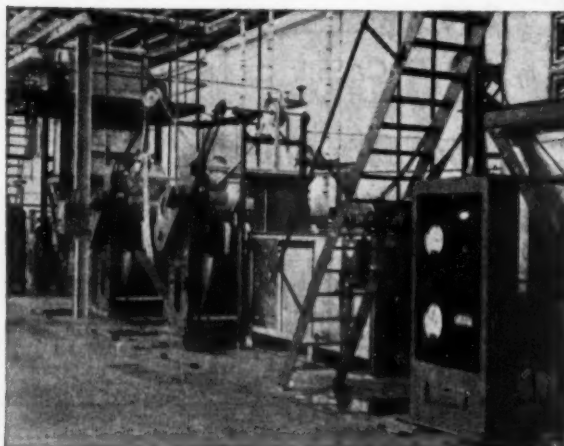
**ADVANCE ANNOUNCEMENT**THE SOCIETY OF DYERS AND COLOURISTS  
LONDON SECTION**THE EIGHTH  
LONDON LECTURE****COLOUR AND DESIGN IN DRESS FABRICS**by **S. J. R. LEEMING Esq**  
Samuel Courtauld & Co Ltd Halstead*will be held at***THE WALDORF HOTEL  
Aldwych London WC2**on **FRIDAY 21 OCTOBER 1960**

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Plant. 'J' boxes fitted with  
Du Pont type heaters



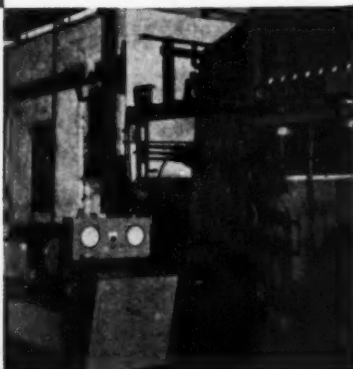
Section of Continuous Pad  
Steam Dyeing Range

Farmer Norton continuous processing plants are made for —

- 1 Any bleaching, dyeing and finishing process.
- 2 Cloth in rope or open width.
- 3 Heavy or light cloth.
- 4 Large or small output.

We make the full range of equipment needed and take full responsibility for complete installations.

Our wide experience is at your service.



# FARMER NORTON

## SIR JAMES FARMER NORTON & CO LTD

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